AN ABSTRACT OF THE THESIS OF

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Title: REACTIVE INTERMEDIATES IN THE TRICYCLO-

[3.2.1.0^{2,4}]OCTANE RING SYSTEM

Abstract approved ___*Redacted for Privacy*___
                        Dr. Peter K. Freeman

An investigation of some potential non-classical carbene and

free radical intermediates in the tricyclo[3.2.1.0^{2,4}]octane ring

system is described.

Methoxide ion-induced decomposition of endo-tricyclo-

[3.2.1.0^{2,4}]octan-8-one tosylhydrazone in anhydrous diglyme at

150-155°, using a 1:5.74 molar ratio of the tosylhydrazone to the

base, gave 11% anti-8-methoxy-endo-tricyclo[3.2.1.0^{2,4}]octane,

1% of syn-8-methoxy-endo-tricyclo[3.2.1.0^{2,4}]octane, 51% of endo-

2-methoxytricyclo[3.3.0.0^{4,6}]octane, 33% of tetracyclo-

[3.3.0.0.^{2,8}0^{4,6}]octane, and 4% of tricyclo[3.3.0.0^{4,6}]oct-2-

ene in a total yield of ca. 80%. The structures of the ethers were

unequivocally established by independent synthesis. The relative

proportions of the ethers were found to increase and those of the

hydrocarbons were found to decrease progressively on addition of

increasing amounts of methanol-0-d to the reaction.

Decomposition of the tosylhydrazone with its imino hydrogen replaced by deuterium yielded 6% of the rearranged endo-ether, 3% of the endo-anti-ether, 81% of the tetracyclic hydrocarbon and 10% of the tricyclic olefin. The observed deuterium isotope effect is consistent with a cationic precursor for the ethers and a carbene precursor for the hydrocarbons. The tetracyclic hydrocarbon formed in the decomposition of the tosylhydrazone-N-d_1 was found to have 23±3% d_1. On the basis of the clear evidence of transannular tris-homocyclopropenyl participation and the rather low deuterium content of the tetracyclic hydrocarbon, it is suggested that the carbene is probably stabilized by non-classical delocalization and leads to the tetracyclic hydrocarbon via a concerted pathway as the major reaction route. The concerted pathway from the delocalized carbene which involves bond formation between C-2 and C-8, fission at C-2-C-4 and bonding between C-4 and C-6, with concomitant hydrogen migration, all taking place in a synchronous fashion, is depictable as $\sigma^2 a + \omega^2 a + \omega^0 a$ process which is symmetry-allowed thermally by the Woodward-Hoffmann rules for pericyclic reactions.

An investigation of the free radical chlorination of exo- and endo-tricyclo[3.2.1.0^{2,4}]octane with t-butylhypochlorite was undertaken. The exo-hydrocarbon on irradiation with t-butylhypochlorite at 40° using a 2:1 molar ratio of the hydrocarbon to the chlorinating

agent, afforded 67% of exo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane, 12% of endo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane, 17% of 1-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane, and 4% of an unidentified product in a total yield of 27%. The epimeric exo- and endo-6-chlorides were synthesized by independent routes to confirm their structures. A mixture of the three monochlorides on reduction with tri-n-butyltin hydride (TBTH) at 95° gave exclusively exo-tricyclo[3.2.1.0^{2,4}]-octane, thus evidencing the presence of this ring system in all the three chlorides. The lack of stereospecific chain transfer of the radical center generated at the 6-position, coupled with its conspicuous failure to undergo skeletal rearrangements clearly militate against its representation as a non-classical delocalized radical.

The endo-hydrocarbon on photochlorination under analogous conditions gave 66% of anti-8-chloro-endo-tricyclo[3.2.1.0^{2,4}]-octane, 27% of endo-2-chlorotricyclo[3.3.0.0^{4,6}]octane, 5% of an incompletely characterized chloride and 2% of an unisolable component in a total yield of 33%. The structure of the endo-anti-8-chloride was confirmed by its stereospecific methanolysis to endo-2-methoxy-tricyclo[3.3.0.0^{4,6}]octane. On dilution of the chain transfer agent, t-butylhypochlorite, the relative proportions of the anti-8-chloride and the rearranged endo-chloride diminished and increased respectively, arguing against the single intermediacy of a non-classical radical. The proportions of the two unidentified minor components

also increased on dilution of t-butylhypochlorite, indicating that they are also possibly the resultants of abstraction at the 8-position. A rapidly equilibrating pair of classical radicals perhaps explains best the observations.

The rearranged radical was generated by two other independent routes. Radical reduction of the rearranged endo-chloride with TBTH yielded the rearranged hydrocarbon, tricyclo[3.3.0.0^{4,6}]octane exclusively. Similar reduction of the rearranged dichloride, endo-2-chloro-5-chloro-tricyclo[3.3.0.0^{4,6}]octane, gave 83% of the tertiary cyclopropyl chloride, 7% of the rearranged endo-chloride and 10% of the rearranged hydrocarbon, tricyclo[3.3.0.0^{4,6}]octane. The lack of reverse rearrangements in both the reductions argue against a single non-classical radical intermediate.

Attempts at synthesis of the endo-syn- and endo-anti-8-chlorides were unsuccessful. Reaction of a 64:36 mixture of the endo-syn-8-ol and the endo-anti-8-ol with thionyl chloride in ether or thionyl chloride and pyridine gave exclusively the rearranged endo-chloride, endo-2-chlorotricyclo[3.3.0.0^{4,6}]octane. Both the endo-syn-8-ol and the endo-anti-8-ol when allowed to react with triphenylphosphine and carbon tetrachloride gave Δ^4-cycloheptenyl carboxaldehyde and the rearranged endo-chloride. The identity of the aldehyde was unequivocally established by its reduction with lithium aluminum hydride to the known Δ^4-cycloheptenylmethyl

alcohol. An ion-pair mechanism is proposed to account for the

formation of the rearranged chloride. The mechanism of the forma-

tion of the aldehyde is discussed. Treatment of endo-tricyclo-

[3.2.1.0^{2,4}]octan-8-one with phosphorus pentachloride in carbon

tetrachloride solution at reflux temperature gave exclusively the

rearranged dichloride, endo-2-chloro-5-chlorotricyclo[3.3.0.0^{4,6}]-

octane.

Photoreaction of endo-tricyclo[3.2.1.0^{2,4}]oct-6-ene with

t-butylhypochlorite in carbon tetrachloride at 40° yielded the trans-

and the cis-t-butylhypochlorite adducts in a 43:57 ratio. Both the

adducts on reduction with TBTH gave exo-6-t-butoxy-endo-tricyclo-

[3.2.1.0^{2,4}]octane exclusively. Subjection of the exo-olefin to similar

photoreaction gave the trans- and the cis-adducts in the ratio 78:22.

Both the adducts on TBTH reduction yielded exclusively exo-6-t-

butoxy-exo-tricyclo[3.2.1.0^{2,4}]octane. Deltacyclene on similar

photoreaction with t-butylhypochlorite gave the trans- and the cis-

adducts in the ratio 85:15. Both the adducts on TBTH reduction

yielded the same exo-8-t-butoxydeltacyclane. There was no evidence

of any monochloride in the reactions of all the three olefins with

t-butylhypochlorite. The lack of stereospecificity of the adducts and

the absence of skeletal rearrangements in all the three cases make it

mandatory to represent all the radical intermediates involved as

simple classical radicals.

Reactive Intermediates in the Tricyclo-
[3.2.1.0^{2,4}] octane Ring System

by

Ramaswamy Srinivasa Raghavan

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BIOGRAPHICAL SKETCH OF THE AUTHOR

Ramaswamy Srinivasa Raghavan was born in Ramnad, Madras State, India, in 1941. He had his secondary education in Rajah's High School, Ramnad, acquitting himself creditably in the S. S. L. C. Public Examination held in March 1956, getting the first rank in the school and was awarded a gold medal. In June 1956 he enrolled in Vivekananda College, Madras (affiliated to the University of Madras) and passed the Pre-University Examination held in April 1957 in First Class with two distinctions. In June 1957 he again enrolled in Vivekananda College and in June 1960 passed the B. Sc. Degree Examination in Chemistry in First Class. That July he got admitted into the M. Sc. Program in Pachaiyappa's College, Madras and in June 1962 passed the M. Sc. Degree Examination of the University of Madras in Second Class. From October 1962 to August 1967 he served Pachaiyappa's College as a Lecturer in Chemistry. In September 1967 he enrolled as a graduate student at the University of Idaho and in September 1968 transferred to Oregon State University. In October 1971 he completed the requirements for the degree of Doctor of Philosophy of which this thesis is a part.

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REACTIVE INTERMEDIATES IN THE TRICYCLO[3.2.1.0^{2,4}]OCTANE RING SYSTEM

I. INTRODUCTION

This thesis describes our investigation of some carbene and free radical intermediates which might exist as non-classical delocalized species. For a full appreciation of our research, an appraisal of earlier work relating to non-classical delocalized carbonium ions is imperative since this provided the necessary impetus for later studies of the possibility of similar delocalized trivalent and divalent carbon intermediates.

One of the most acrimonious controversies in organic chemistry is that pertaining to non-classical carbonium ions. A little over two decades ago, Winstein and Trifan (1, 2) observed that _exo_-2-norbornyl brosylate underwent acetolysis 350 times faster than the _endo_-isomer. The product acetate from both was the _exo_-isomer, the one from the _exo_-isomer being completely racemic and that from the _endo_-isomer being extensively racemized.
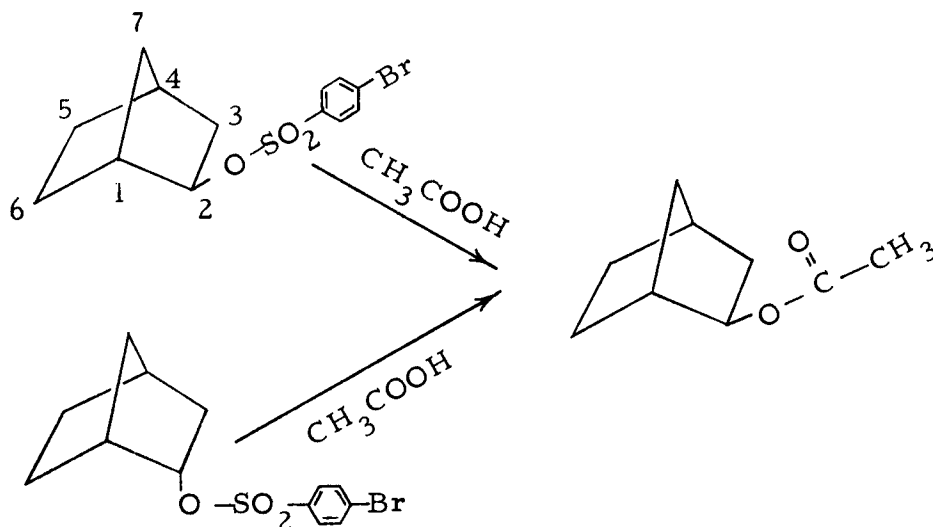
To explain the augmented rate of solvolysis of the exo-isomer,

Winstein postulated the participation of the C_1-C_6 bonding electron

cloud in the ionization process, which is possible due to favorable

geometry in the exo-isomer but not in the endo-isomer. Thus the

exo-brosylate was thought to form directly the non-classical delocal-

ized carbonium ion 1.
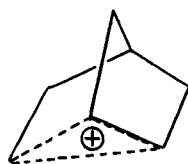
1

Winstein suggested that the endo-isomer could form a classical ion

initially which might then rearrange to the presumably more stable

bridged cation.

Hardly could Winstein have anticipated that his postulation of

a non-classical carbonium ion would open the floodgates of a major

controversy in mechanistic organic chemistry. Brown has criticized

this postulation and has asserted that all the experimental observa-

tions could be accommodated by considering a pair of rapidly equi-

librating classical carbonium ions (3-7).
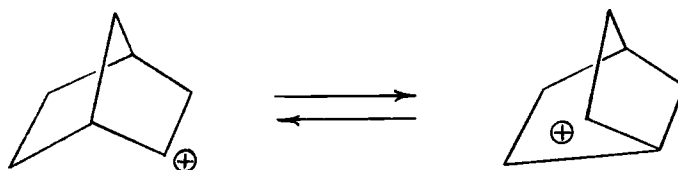
Brown suggests that the ionization of the exo-isomer could proceed

at a normal rate while that of the endo-isomer could be abnormally

slow, owing to steric hindrance to departure of the endo-leaving

group due to the endo-hydrogens on C_5 and C_6. There have thus

developed two schools of thought concerning carbonium ions, the

votaries of one school favoring the non-classical tenet and the adher-

ents of the other school clinging tenaciously to the classical viewpoint.

In a vigorous drive to vindicate their stand, the protagonists

of the non-classical school investigated the possibility of non-classical

carbonium ion formation in a plethora of ring systems. The result

has been a scintillating proliferation of experimental observations.

An analysis of these studies led Schleyer to propose some well-

defined criteria of non-classicality (8). These include rate accel-

eration when the precursor geometry is suitable, high stereospecificity

of kinetically controlled products, and a pronounced tendency towards

rearrangement. Of these, observed Schleyer, only rate enhancement

can serve to distinguish between a pair of rapidly equilibrating clas-

sical carbonium ions and a single non-classical ion.

It would be appropriate to present here some of the reported

studies which spotlight the inadequacy of the classical viewpoint.

Winstein and his co-workers (9-11) observed that anti-7-norbornenyl

tosylate 2 solvolyses 10^{11} times faster than 7-norbornyl tosylate and

forms exclusively anti-7-norbornenol 3. The authors attribute the

$$\text{2} \xrightarrow{\text{50\% aq. acetone}} \text{3}$$

2   3
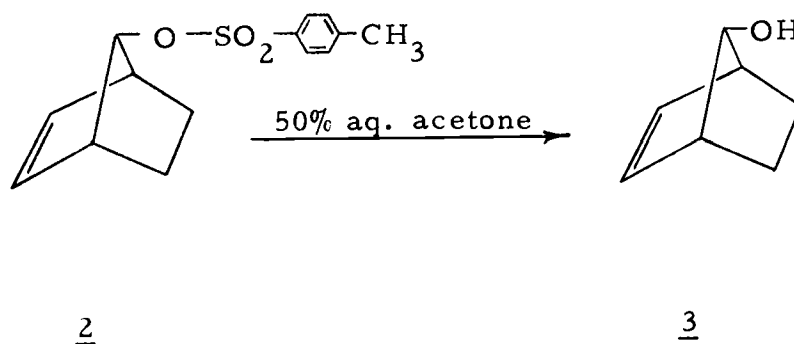
enormous rate enhancement to the stabilization of the incipient

positive charge on C_7 by the π-electrons of the double bond. The

location of the π-orbital on the backside of the leaving group is

eminently conducive to this p-π interaction which leads to the inter-

mediate ion 4.

4
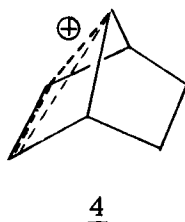
This would also easily explain the solitary product of retained configuration. The possibility that the anchimeric assistance could be due to widening of the C_1-C_7-C_4 bond angle has been shown to be virtually untenable by Tanida and his co-workers (12-14) as a result of their study of substituent effects in the benzene ring in the benzonorbornenyl system. Incorporation of methoxy and methyl substituents at the 6-position increase the rates of acetolysis of the anti-9-brosylate 5
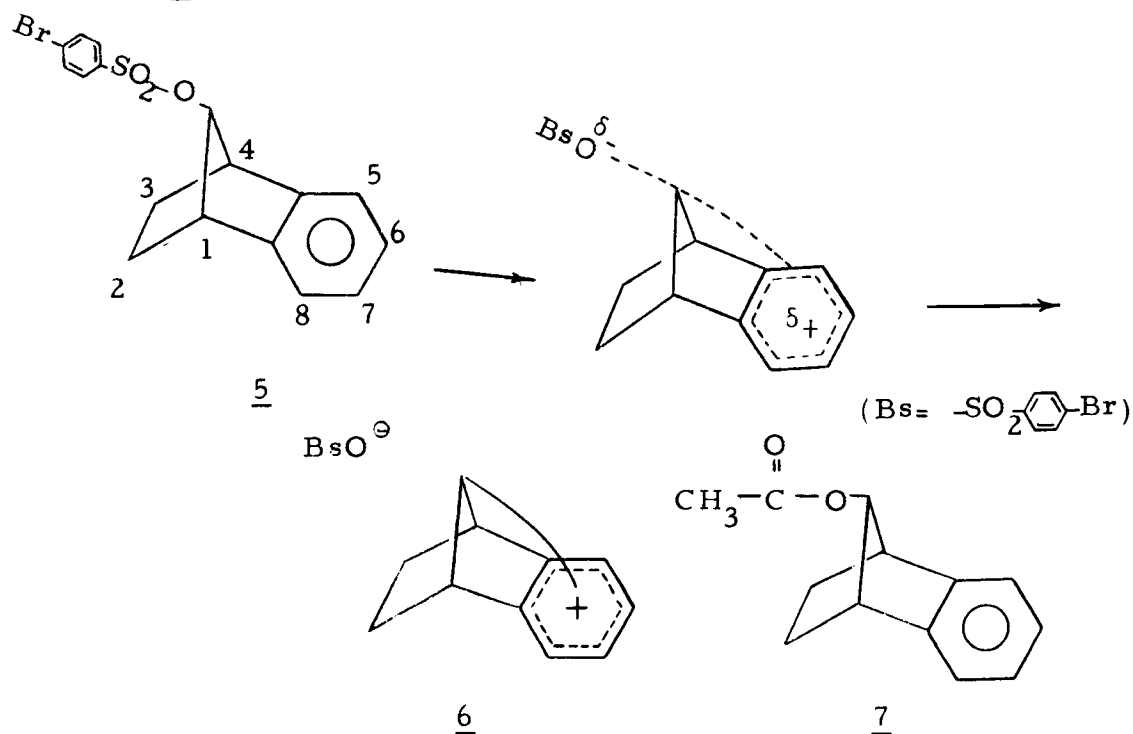
by factors of 53.7 and 5.7, respectively. The chloro, bromo, and nitro substituents retard acetolysis by factors of 0.045, 0.030, and 1.4×10^{-4}, respectively. The magnitude of the substituent effects can be seen dramatically from the fact that $k_{CH_3}/k_{NO_2} = 386,000$.

$$\frac{k_{OCH_3}}{k_{NO_2}} = 386,000$$
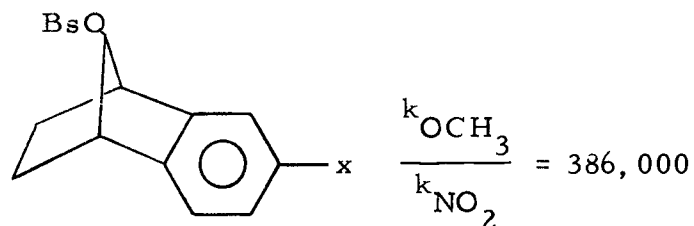
These results led Tanida to conclude that if the bond angle effect

does exist, it must be relatively unimportant.

The non-classical school added another glittering feather to

its cap when three groups of workers simultaneously reported their

solvolytic studies on the tricyclo[3.2.1.0^{2,4}]octane ring system

(14-17). The relative rates of solvolysis as reported by these

authors are given below:
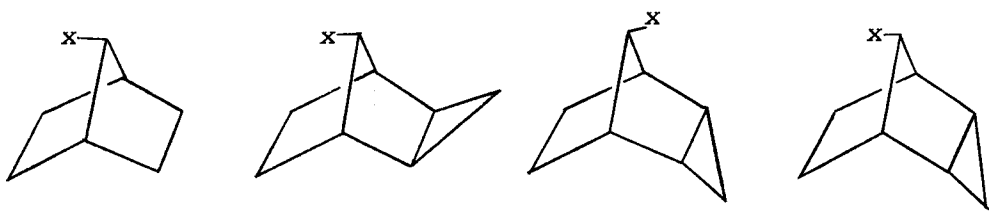
Relative Rate
of Solvolysis: 1   0.4   15   10^{14}

25%   75%
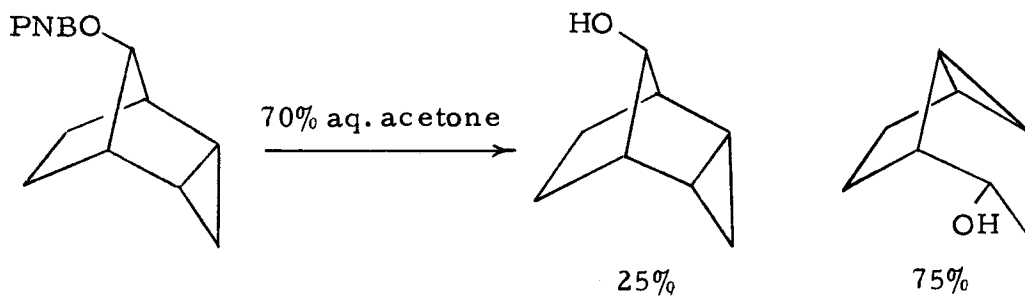
Inspection of the rate data clearly reveals that the exo-orientation

of the cyclopropane ring has virtually no effect on the relative rate

of solvolysis. The endo-anti isomer, on the other hand, solvolyses

with an unprecedented degree of anchimeric assistance. Complete

stereospecificity of the products has also been demonstrated by the

authors. Backside participation by the cyclopropane ring in the

ionization of the endo-anti isomer leading to the formation of the

2, 4-ethanotrishomocyclopropenyl cation as suggested by the authors,
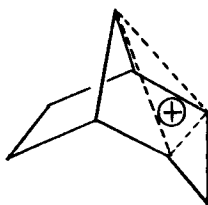
is the most plausible explanation. σ-type interaction of the elec-

tronically deficient cationic center with the sp^5 orbitals of suitably

oriented cyclopropane is clearly more effective in promoting ioniza-

tion than the p-π-overlap in the case of the anti-7-norbornenyl cation.

The classical school has not so far offered any convincing explanations
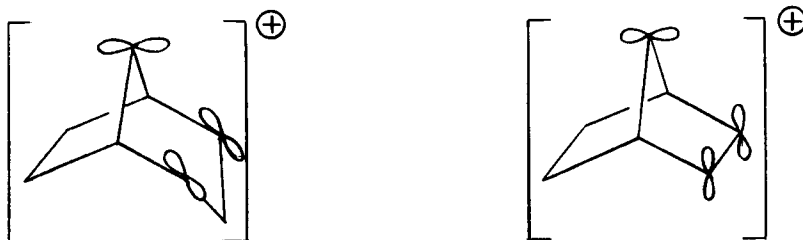
for the above cases. There remained, however, the possibility,

albeit remote, that the anchimeric assistance could arise from relief

of strain on conversion to the rearranged system. In this regard,

an experimental observation of considerable significance was

reported by Coates and Kirkpatrick (18). These workers observed

that the solvolysis of pentacyclic p-nitrobenzenesulfonate 8 occurs
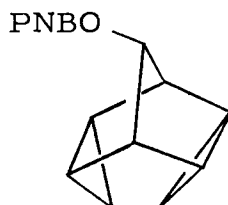
8

10^{12} times faster than that of the 7-norbornyl derivative and that the

major solvolysis product has the same ring structure as the starting

material, though a triply degenerate rearrangement occurs. The

greatly enhanced rate could not then be attributed to an overall relief

of strain.

While the non-classical carbonium ion has been the subject of

controversy non pareil in organic chemistry, some workers embarked

on an exploration of similar non-classical delocalized carbene and

free radical intermediates. A carbene or divalent carbon is iso-

electronic with its trivalent cationic analog. It is linked to two

adjacent groups by covalent bonds and has two non-bonding electrons

which may have their spins antiparallel (singlet) or parallel (triplet)

(19). A singlet carbene, with its sp^2 hybridization is believed to

have a planar trigonal arrangement with the valency angle close to

120°. This species has no unpaired electrons, has a vacant p
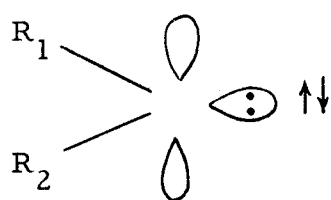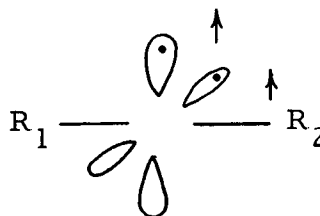
Singlet Carbene   Triplet Carbene

orbital as in carbonium ions, and can be regarded as "a superimposition of a carbonium ion and a carbanion" (20). The triplet carbene is believed to involve sp hybridization, with a nearly linear arrangement of groups and the valency angle is in the neighborhood of 180° (20, 21). The common reactions of carbenes are insertion into σ -bonds and addition to multiple bonds, with triplet carbenes behaving especially in a radical-like fashion.

Recently Hoffmann and Gleiter (22) on the basis of extended Huckel calculations predicted that there is a definite probability of singlet, stabilized, non-classical carbenes in favorable cases. For example, in the case of 7-carbenanorbornene 9, which cannot undergo intramolecular addition to the double bond, since the product would be an extremely strained molecule which has one carbon with all four bonds on one side of a plane, the system might choose an intermediate geometry 10 in which the bridge methylene is bent part way over (the "foiled methylene"). This interaction should stabilize the
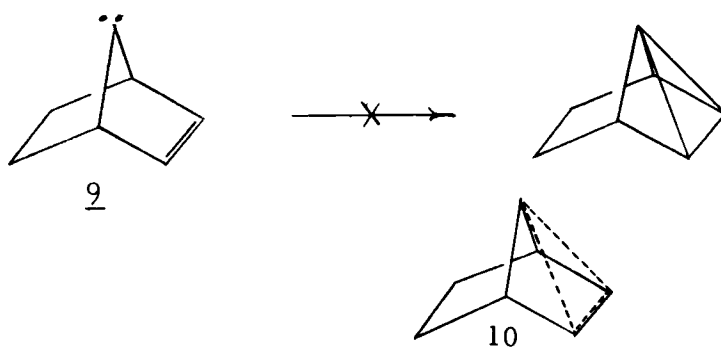
singlet ground state, though the intramolecular addition resulting in

cyclopropanation of the double bond is sterically forbidden. Hoffmann

predicts that the interaction of a suitably oriented cyclopropane ring

(as in 11) with the carbene center results in a deeper potential energy

minimum, indicating greater stabilization.
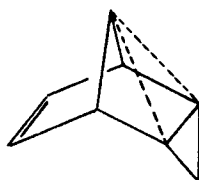
These predictions have served to provide added stimulus to workers

engaged in carbene chemistry, especially in bridged polycyclic

systems.

One would be tempted to conjure up the vision of a delocalized

2-carbenanorbornane by analogy to the 2-norbornyl cation. However,
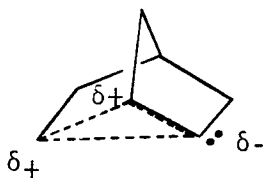
the reported behavior of this carbene, studied by Reusch and his

co-workers (23) does not throw any light on this problem, as it undergoes exclusive γ-insertion to give nortricyclene.

It would be instructive to describe here the reports of several other workers on carbene studies in bridged polycyclic systems. 7-Carbenanorbornane 12 undergoes γ-insertion and a 1, 2-carbon
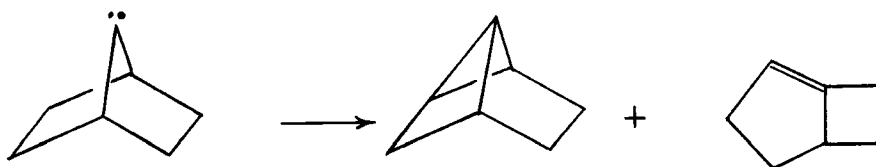
12

shift yielding tricyclo[3.2.0.0$^{2, 7}$]heptane and bicyclo[3.2.0]hept-1-ene (24). 5-Carbenanorbornene 13, studied by Freeman, George and

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Rao (25) gives norbornadiene as the sole volatile product, arising from 1, 2-hydrogen migration. No evidence of homoallylic interaction of the double bond was observed.

In another interesting attempt to observe non-classical stabil-
ization of a carbene intermediate, Freeman and Desai (26) studied
the reactions of exo- and endo-5-norbornenyl carbene intermediates.
The exo- species 14 yielded 5-methylenenorbornene and exo-tricyclo-
[3. 2. 1. 0$^{2, 4}$]oct-6-ene in the ratio 23:76. The ratio of hydrogen
migration to insertion in this case is close to the value found for
cyclopentyl carbene (27. 5:72. 5) by Kirmse and Wachterhauser (27).
The endo-carbene 15, on the other hand, gave 5-methylenenorbornene
and endo-tricyclo[3. 2. 1. 0$^{2, 4}$]oct- 6-ene in the ratio 57:42 (hydrogen
migration:insertion). The saturated exo-carbene gave 2-methylene-
norbornane and exo-tricyclo[3. 2. 1. 0$^{2, 4}$]octane in the ratio of 11:89.

14   23%   76%

CH: CH$_2$

15   57%   42%
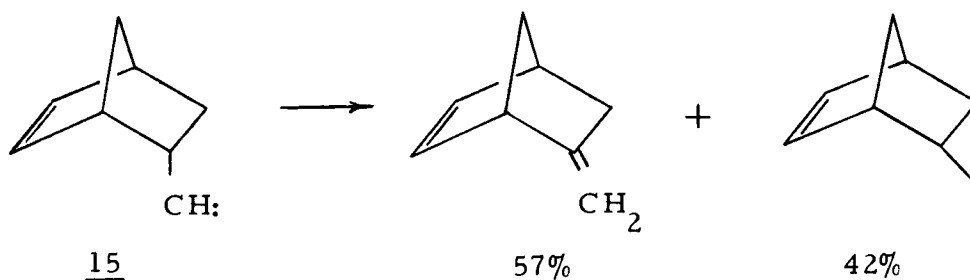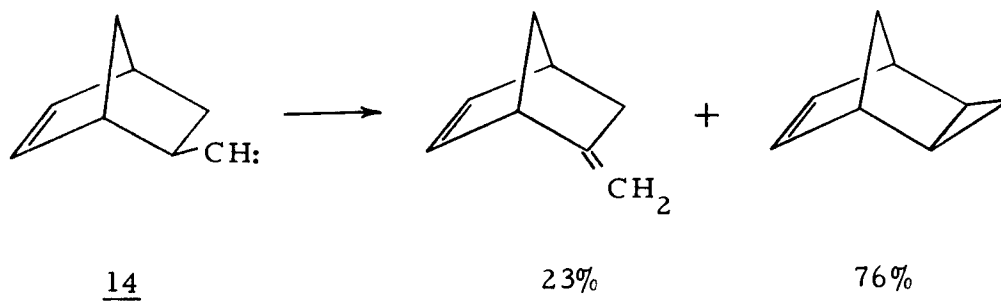
The saturated <u>endo</u>-carbene yielded 2-methylenenorbornane, <u>endo</u>-tricyclo[3.2.1.0^{2,4}]octane, and bicyclo[3.2.1]oct-2-ene in the ratio 41:55:4. Thus the ratios of hydrogen migration to insertion are quite similar for norbornenyl- and norbornylcarbene intermediates of similar geometry. Hence the role of the double bond in altering the ratios of hydrogen migration to insertion in the epimeric carbenes seems to be a very minor one. Another interesting point to note is that while the saturated <u>endo</u>-carbene undergoes some ring expansion to give bicyclo[3.2.1]oct-2-ene, the unsaturated <u>endo</u>-carbene fails to display this behavior. Inspection of models shows that alignment of the p orbital in the unsaturated <u>endo</u>-carbene for maximum overlap with the π-bond system provides an alignment which is detrimental to ring expansion. It is possible that there is some non-classical stabilization in this carbene, but the evidence is not compelling.

Intent on studying the possibility of cyclopropane interaction of the trishomocyclopropenyl type in a carbene intermediate, Freeman and Kuper (28) generated 3-carbenabicyclo[3.1.0]hexane <u>16</u> and found that there was no evidence of such interaction, the only product being

<u>16</u>
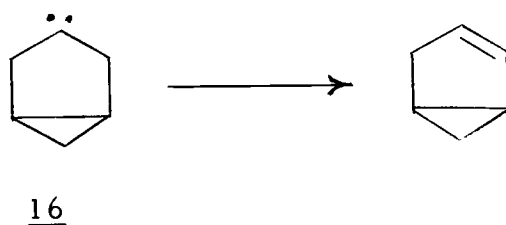
bicyclo[3.1.0]hexene-2, resulting from 1,2-hydrogen migration. A few years later, Freeman and Balls (29, 30) reported that a similar

fate overtook 8-carbenadeltacyclane 17 and no cyclopropane participation analogous to that found in the cationic analog (31, 32) was observable. These instances pinpoint the fact that 1, 2-hydrogen migration is a major impediment in the study of possible non-classical carbenes and should hence be eliminated in order to facilitate such a study.

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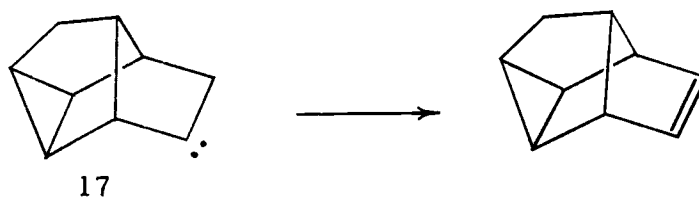
In an effort to circumvent this difficulty, Freeman and Kuper (33) undertook a study of exo-8-carbenatricyclo[3.2.1.0^{2,4}]octane 18 in which the 1,2-hydrogen migration is prohibited by virtue of Bredt's rule. This species undergoes a deep-seated rearrangement leading to bicyclo[3.3.0]octa-1,6-diene and a mixture of isomeric bicyclo[3.3.0]octadienes in the ratio 65:35. The mechanism of the formation of the dienes is uncertain but the authors suggest two possible reaction courses; migration of C-2 (18 → 19 → products), with 19 undergoing either a concerted (σ^2s + σ^2a fission at bonds a or at bonds b) or biradical ring opening to products (fission at a, b, or c) or migration of C-7 (18 → 20 → products) with 20 undergoing a vinylcyclopropane rearrangement to 21 and 21 opening by a partly concerted (fission at bonds a), partly biradical (fission at b or b + a)

18   19   +

18   20   21
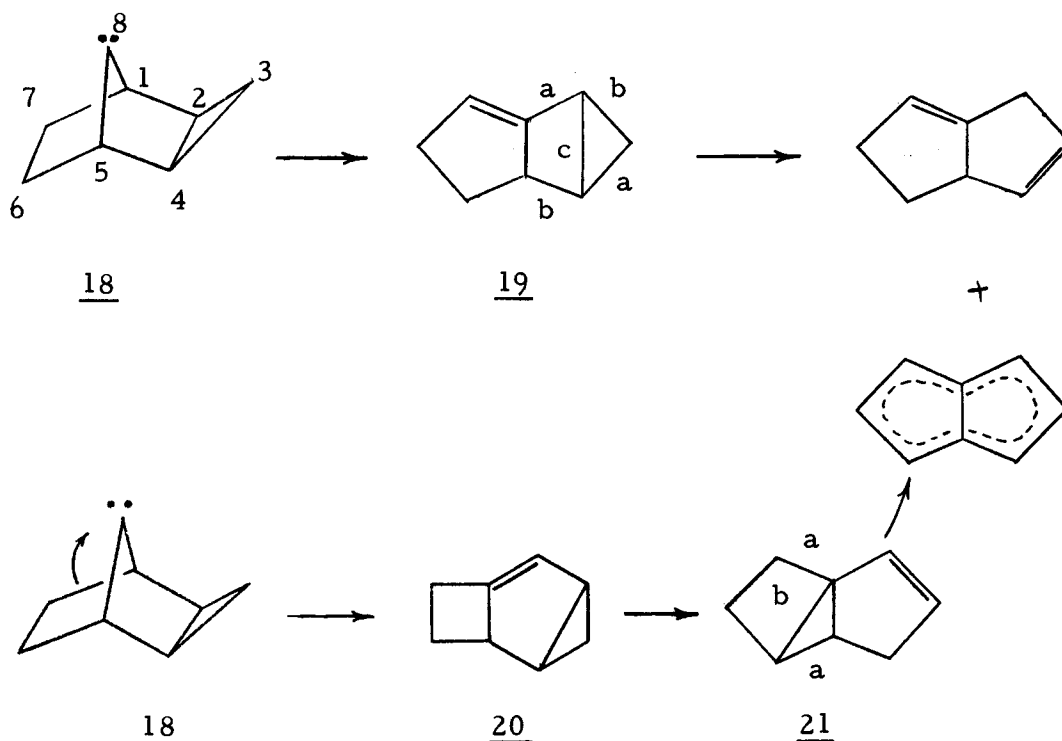
or a completely biradical process. It is significant to note that no

transannular cyclopropane interaction was observed. This result

is not surprising in view of the reported behavior of the cationic

analog (15-17, 34).

Another case of a carbene which cannot undergo 1, 2-hydrogen

transfer but nevertheless yields no evidence of non-classical delocal-

ization is the species 22 reported by Freeman, Rao and Bigam (35).

This divalent carbon intermediate undergoes exclusive transannular

22   35%   65%
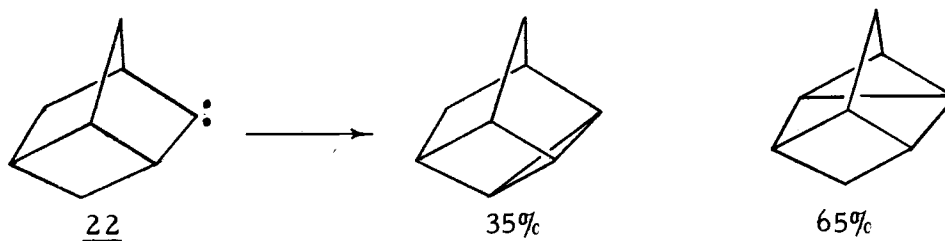
insertion giving two tetracyclooctanes. These reports highlight the fact that prevention of 1, 2-hydrogen migration, though necessary, has not been sufficient so far to allow the observation of non-classical character in carbenes.

An instance of apparent non-classical stabilization of a carbene intermediate was reported recently by Fisch and Pierce (36). These workers observed that the carbene 23 generated by decomposition of the sodium salt of the tosylhydrazone of the related ketone yields tetrahydroindene 26 as the major product, accompanied by consider-able amounts of the tricyclic olefins 24 and 25. The C-H bonds favorable for insertion are the axial C-H bonds on C-4, C-7, and C-8 as these are in the required syn-periplanar relationship with the carbene center. Of these, the allylic bond (C-4) would be the most reactive and so one would expect 28 to be the major cyclopropyl olefin among the products. In case of rearrangement, migration of the allylic bond would be expected to predominate, resulting in 27 rather than 26. On the other hand, if there is interaction of the double bond entailing non-classical stabilization, some deformation of the cyclohexene ring would be required to bring C-9 closer to the double bond. This would result in the axial hydrogen at C-4 moving away from the stereochemically favorable syn-periplanar position, and favor the non-allylic cyclopropyl olefins 24 and 25. Further the interaction with the double bond may result in an increased extent

23   24   25

18%   18%

26   27

31%

28
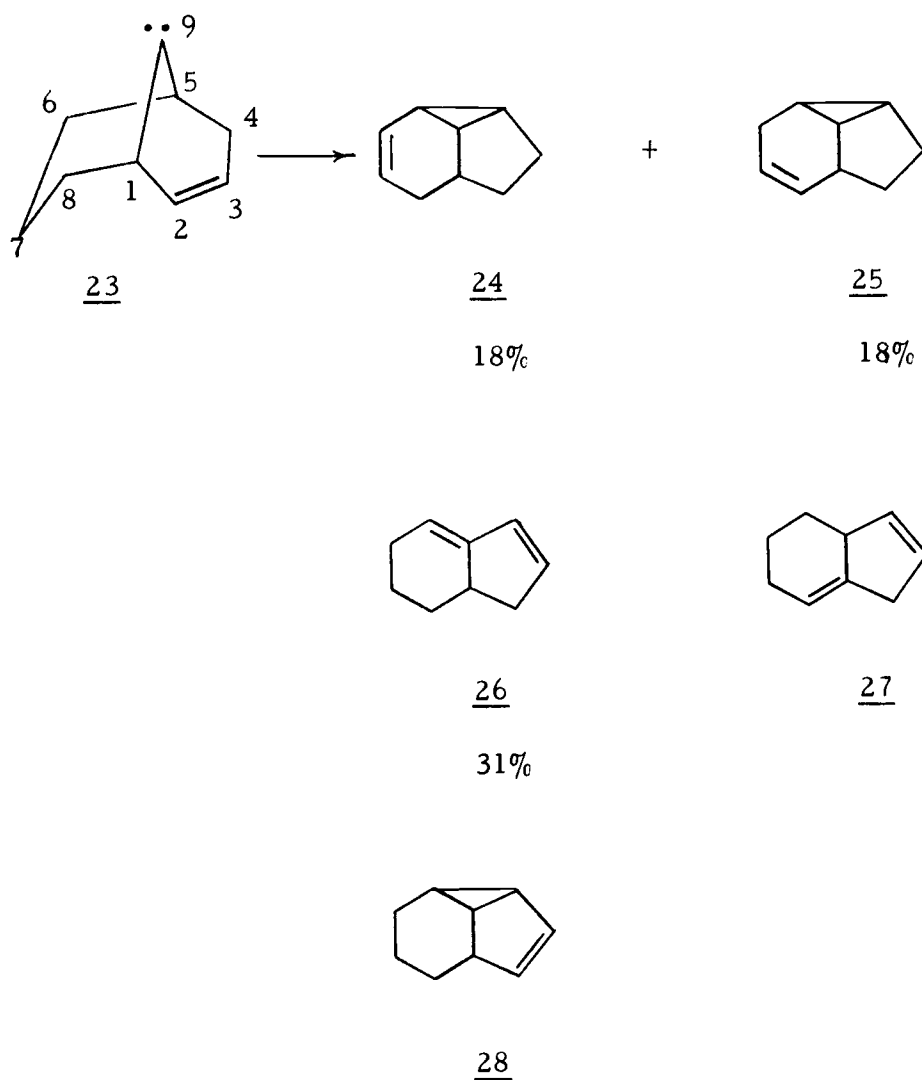
of migration of C-2 to yield 26. The experimental results support the latter alternative. The evidence is strongly suggestive of double bond interaction with the carbene center but is not dramatically con-clusive.

Moss and his co-workers (37) have recently reported on the intermediate 7-carbenanorbornene 9. This species, generated by vacuum pyrolysis of the lithium salt of the corresponding

tosylhydrazone, gave bicyclo[3.2.0]heptadiene-1,6, 29, as the major

product, accompanied by spiro[2,4]heptadiene 30 as the chief minor

product and smaller amounts of additional minor products as shown.

9   29   30   31   +

67%   6.9%   2.3%

32   33

1%   0.9%
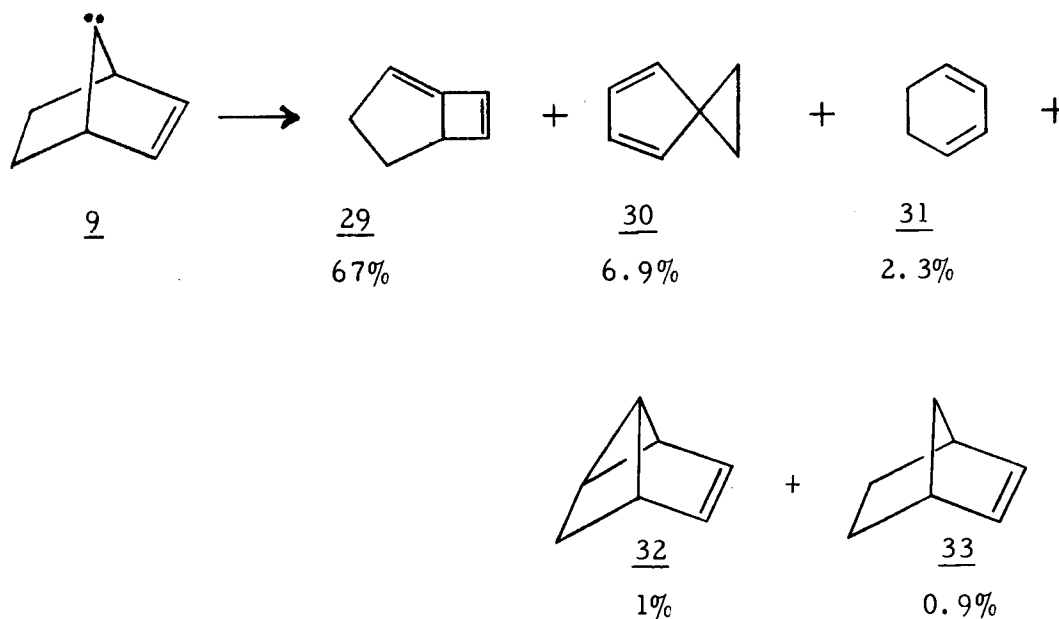
The authors suggest the possibility of a non-classical carbene which

could explain the formation of 29, perhaps via the dipolar species 34.

The "foiled methylene" adduct 35 has been suggested as a possible

fleeting intermediate. A 1,7-vinyl shift is an alternative route to 29.

30 could have resulted from 36, formed possibly by migration of the

ethano bridge of 9. A retro Diels-Alder reaction of the carbene 9

to give cyclopentadienylidene and ethylene, followed by cyclopropana-

tion, provides another route to 30. Further detailed reports are

awaited in order to establish or throw overboard the intermediacy

of the non-classical carbene in this case.

36   9   34   29

30   35
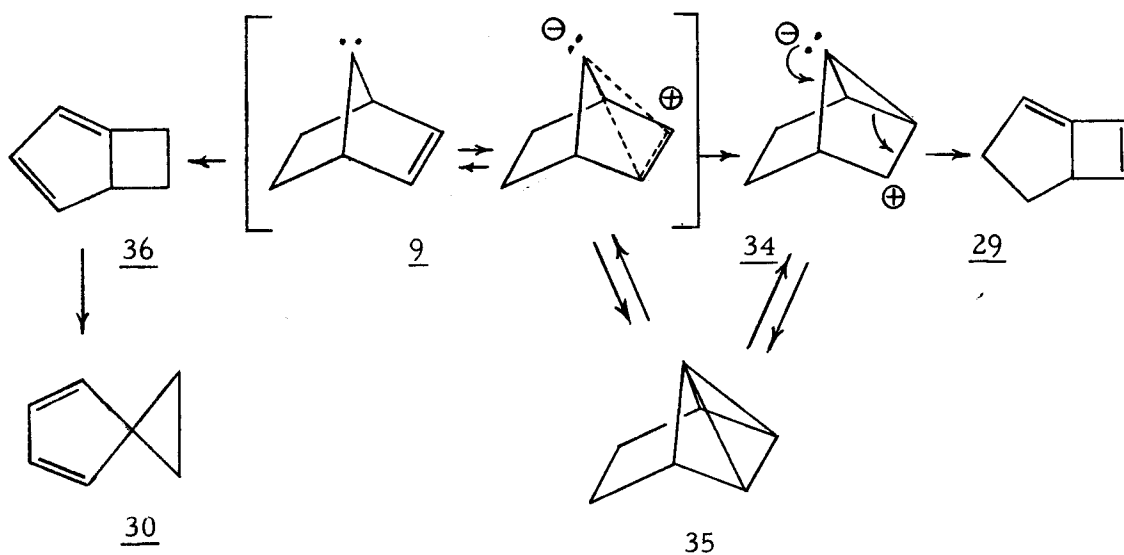
In refreshing contrast to the sparseness of the literature on

non-classical carbene chemistry, we are confronted with a legion

of reports on studies of potential non-classical free radicals. Before

we dwell at length on this interesting subject, a few comments on the

geometry of radicals would be in order. Two structures are possible

for simple alkyl radicals (38-40). The radical carbon could be in a

state of sp^2 hybridization with the odd electron in a p-orbital, thus

entailing a planar configuration. Alternatively, sp^3 hybridization

might be involved placing the odd electron in an sp^3 orbital, which

would make the structure pyramidal. The well known loss of optical

activity when a radical is generated at an asymmetric carbon and a

considerable body of e.p.r. and electronic spectral data are consis-

tent with a planar configuration. On the other hand, the ease of

formation of bridgehead radicals in which the trivalent carbon is situated at the bridgehead of rigid polycyclic ring systems renders the postulation of pyramidal configuration for such radicals inescapable. It appears possible that the energy barrier between the two configurations is low. An important consequence of this versatility of radicals is that anchimeric assistance in radical formation, if observed, could not be attributed to bond angle strain.

It is well-nigh impossible to attempt a complete coverage of the literature on studies of potential non-classical free radicals in this brief introduction. A few reports germane to our work will be discussed in sufficient detail here.

The possibility of a bicyclic, bridged radical 37 analogous to the bicyclobutonium ion intermediate (41) stimulated the study of the

$$CH_2 \text{———} CH_2$$
$$CH_2 \text{— — — —} CH_2$$

*
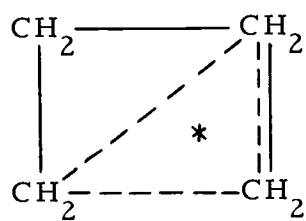
<u>37</u>

cyclopropyl carbinyl radical. Roberts and his co-workers (42) studied the vapor phase photochlorination of methyl-^{13}C-cyclopropane and observed that the products were cyclopropyl carbinyl chloride and allylcarbinyl chloride with no evidence of ^{13}C label scrambling.

$$\triangleright\!\!-^{13}CH_3 \xrightarrow[h\nu]{Cl_2} \triangleright\!\!-^{13}CH_2Cl + ClCH_2\text{-}CH_2\text{-}CH={}^{13}CH_2$$
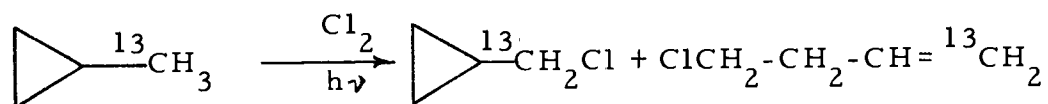
The lack of label scrambling and the absence of cyclobutyl chloride

militate against the intermediacy of equilibrating bicyclic, bridged

radicals of the type 37. The observations could be satisfactorily

explained by considering a pair of simple classical radicals 38 and

39. The homoallylic radical 40 could also explain the data and

$$\triangleright\!\!-\overset{*}{C}H_2 \;\; \rightleftharpoons \;\; \overset{*}{C}H_2\text{-}CH_2\text{-}CH={}^{13}CH_2$$

38   39

$$\begin{array}{c}
\overset{*}{C}H_2 \cdots \\
| \quad\quad CH ----- \overset{*}{C}H_2 \\
CH_2
\end{array}$$

40
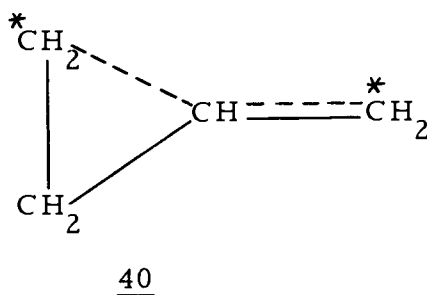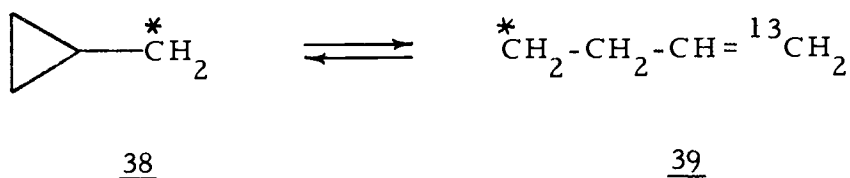
there is no evidence to sustain or rule out this intermediate.

Walling and Fredericks (43) studied the photochlorination of

methyl cyclopropane with t-butylhypochlorite and found that the

products were composed of cyclopropyl carbinyl chloride, allyl-

carbinyl chloride and cyclobutyl chloride, with the proportion of

the ring-opened product decreasing with decreasing temperature.

| 68° : | 28% | 20% | 10% |
| 0° : | 42% | 4% | 9% |
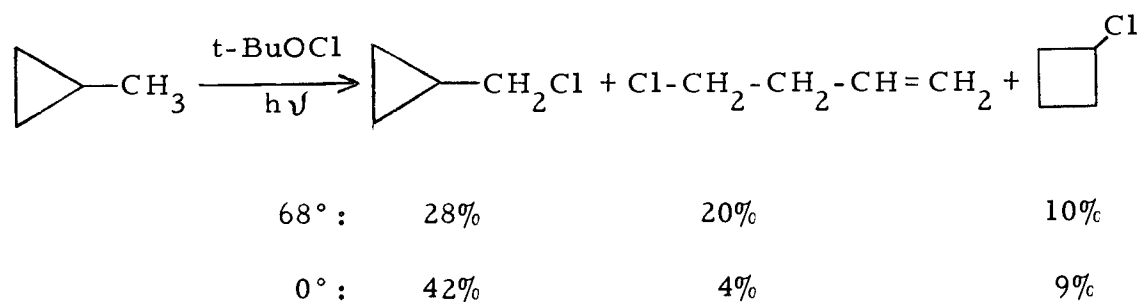
It was concluded that the cyclobutyl chloride resulted from an irreversible rearrangement of the allylcarbinyl radical since the chlorination of cyclobutane did not yield any allylcarbinyl chloride. These results parallel those of Roberts et al. and could be readily explained by suggesting a pair of equilibrating cyclopropyl carbinyl and allylcarbinyl radicals.

Contemplating the possibility of non-classical radicals 42 and 43, Freeman and his co-workers (44) studied the photochlorination of bicyclo[3.1.0]hexane 41 with t-butylhypochlorite. Abstraction at C-2 might conceivably produce 42 while abstraction at C-3 might result in 43.
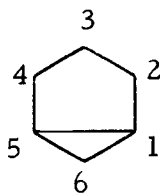
41

42

43

The composition of the products is as follows:
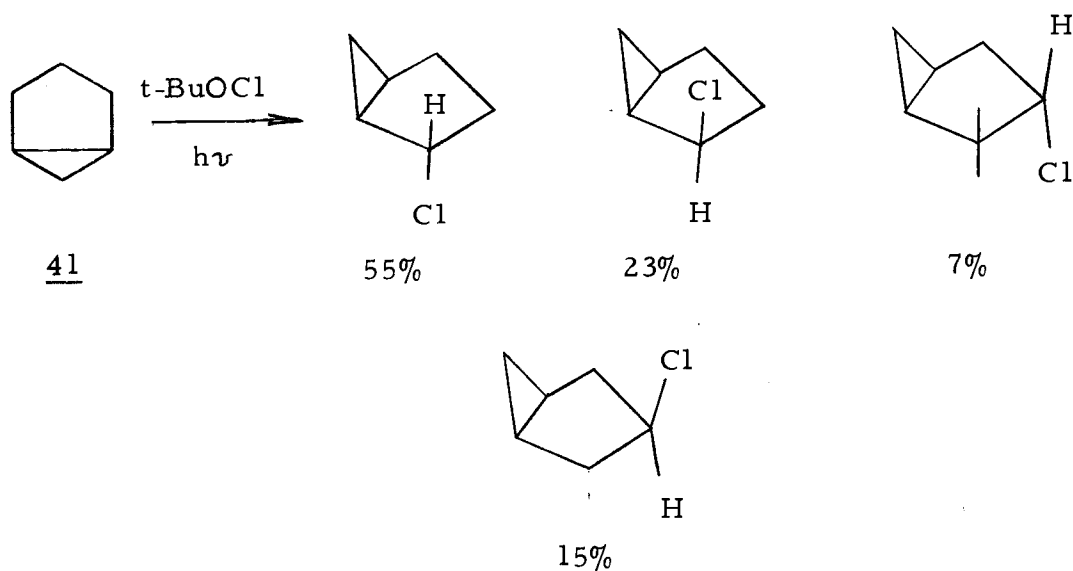
Abstraction at C-2 predominated over abstraction at C-3 notwithstanding the electron-withdrawing inductive effect of the cyclopropane ring which would promote C-3 rather than C-2 abstraction. Freeman attributes this to the resonance effect of the cyclopropane ring. The explanation is offered that since the t-butoxy radical is an electrophilic species, the transition state for abstraction would be expected to be polarized conferring some carbonium ion character on the developing hydrocarbon moiety, which would favor C-2 abstraction. The predominance of the trans-2 chloride is readily understandable as the cis-face is sterically blocked by the cyclopropane methylene. However, the predominance of the cis-3 chloride over the trans-3 chloride is intriguing for the same reason. It is possible to explain this observation by assuming the intervention of the non-classical

radical 43 as one of the intermediates but this reasoning is open to

debate. In a complementary study, Freeman and his co-workers (45)

generated radical centers at C-2 and C-3 in the bicyclo[3.1.0]hexane

skeleton by the radical addition of methanethiol to bicyclo[3.1.0]-

hexene-2 and concluded that simple classical radicals and steric

considerations would suffice to explain the formation of the various

adducts.

A parallel study of the photochlorination of norcarane 44 with

t-butylhypochlorite was recently reported by Boikess and his co-

workers (46). The products were observed to consist of 45 (24%),

cis-46-Cl (8%), trans-46-Cl (23%) and 47-Cl (45%). It was shown

that 47 was the result of rearrangement of 48 under the conditions
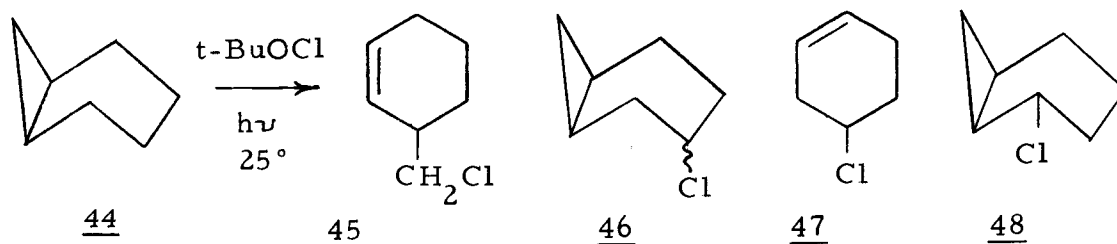
of vpc analysis. Here again the major position of abstraction is

C-2, attributable to resonance stabilization of the 2-norcaranyl

radical or attraction between the electrophilic attacking radical and

the nucleophilic cyclopropyl ring.

A flood of light was shed on the nature of the 2-norbornyl rad-

ical by the work of Cristol and his group of workers (47-49). These

authors carried out extensive studies of the free-radical addition of

p-thiocresol and p-tosyl chloride to some norbornenes. The reaction

of norbornene with p-thiocresol gave exclusively <u>exo</u>-2-norbornyl

thioether. The product that would be expected from rearrangement,

viz. 7-norbornyl thioether was not observed. This led Cristol to
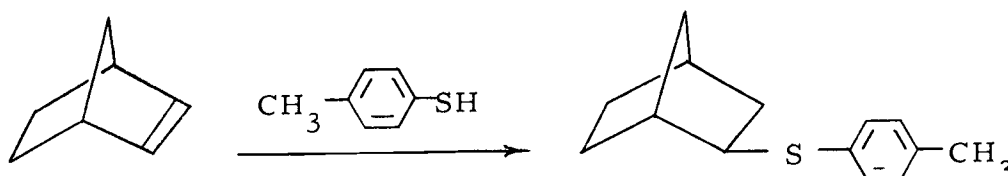
suggest that his results could be more logically explained by postula-

tion of a classical radical intermediate. This is in contrast to the

case of the equivalent cation. Cristol opines that the greater electron

deficiency of the cationic center, compared to the radical, provides

the necessary impetus for bond delocalization in the former. The

radical, by virtue of its possession of an additional electron does

not have so serious an electron deficiency and hence carbon-bridging

mechanism is unlikely. An even better appreciation of the lack of

carbon-bridging in radicals can be gained by consideration of the

molecular orbital principles for three-carbon bridged (cyclopropenyl)

structures (50). The three orbitals for the three-atom structure com-

prise one bonding orbital and two degenerate antibonding orbitals.

Placement of electrons in antibonding orbitals raise the energy of

the system and hence destabilize the system. In the case of the

cation, the two electrons present can be accommodated in the lowest

bonding orbital. The radical has one more electron which has

(a)
Carbonium ion
(2 electrons)

(b)
Radical
(3 electrons)

(c)
Carbanion
(4 electrons)

Energy
Zero
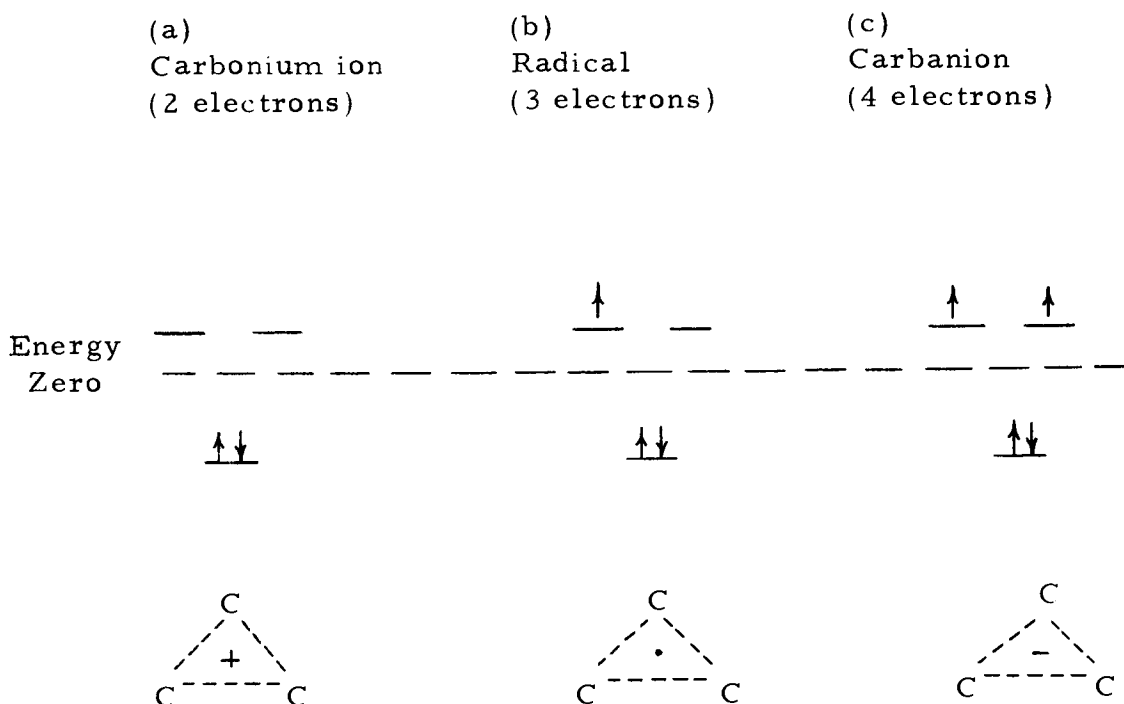
necessarily to go into one of the two antibonding orbitals. In the

case of the carbanion which has two electrons more than the cation

has, both the additional electrons have to go into the antibonding

orbitals. It is hence easily seen that the carbanion would suffer

even more destabilization than the radical.

Cristol and his coworkers further observed that norbornene

was 45 times as reactive as cyclohexene towards the thiocresoxy

radical. This enhanced rate could well be due to relief of strain in

the starting norbornene. The possibility of the sulfur-bridged inter-

mediate 49 was ruled out by the observation that 6-chloroaldrin under-

went exclusive cis-addition.

27
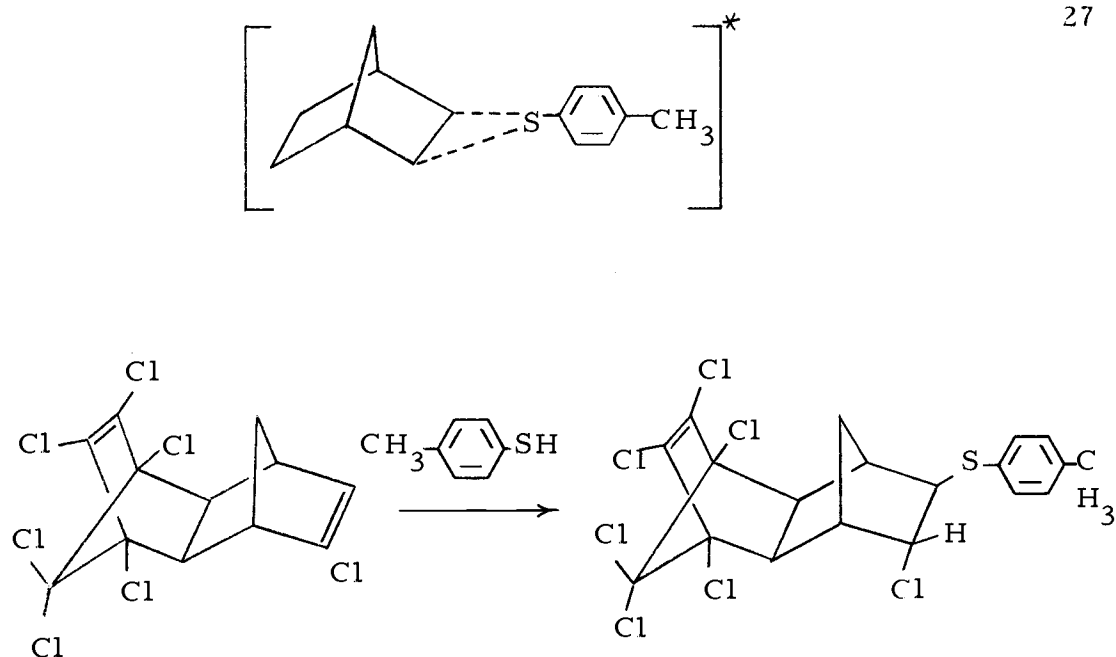
With p-tosyl chloride, norbornene gave almost completely the trans-adduct. Aldrin similarly gave the trans-adduct. These results are obviously incompatible with a non-classical radical which would be expected to give the exo-cis-adduct. The intermediate in this case is a classical radical and the direction of chain transfer is controlled apparently by steric factors.
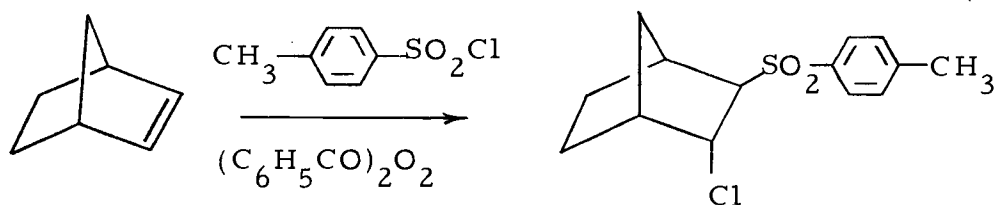
Much water has flown under the bridge since these pioneering studies of Cristol. The 2-norbornyl radical has been generated by several other workers and the weight of evidence argues overwhelmingly against the non-classical radical. Brace (51) observed that the

free-radical addition of iodoperfluoropropane to norbornene and

aldrin gave almost exclusively the respective trans-adducts. Here

again the direction of chain transfer is obviously controlled by steric

factors.

Equally revealing is the report of Kooyman and Veger (52) on

the free radical halogenation of norbornane. On subjection to radical
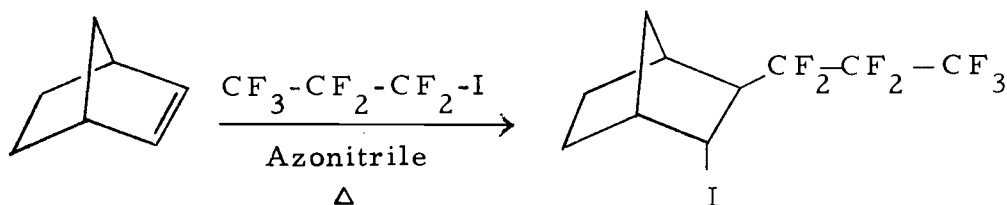
halogenation with a variety of halogenating agents, norbornane yielded

the 2-halides as the major products, the exo-isomer predominantly.

The $\frac{2\text{-exo}}{2\text{-endo}}$ product ratio was found to vary with the nature of the

halogen donor. The predominance of the exo-isomer was explained

as due to the lower accessibility of the halogen donor to the endo-face

than to the exo-face owing to the shielding effect of the methylene

group in the 5 and 6-positions. In accordance with this view, it was
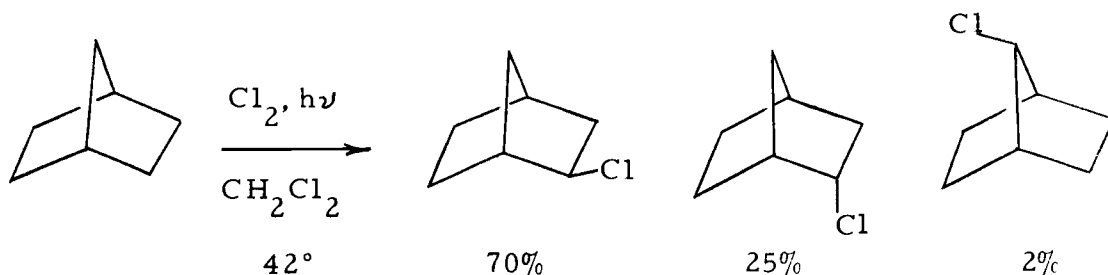
found that the small halogen molecules gave appreciable proportions

of the endo-isomer while bulkier reagents yielded smaller percentages

of this isomer.

No less adverse, from the non-classical point of view, was

the fate in store for the 5-norbornenyl radical. Cristol and his

associates (53) reported that the reaction of norbornadiene with

p-thiocresol gave a 40:60 mixture of norbornenyl and nortricyclyl

thioethers. This result could be explained by considering two pos-

sible reaction routes: (a) reaction via an equilibrating pair of
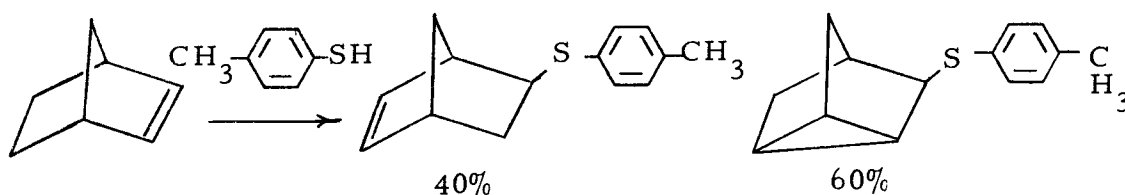
classical radicals, or
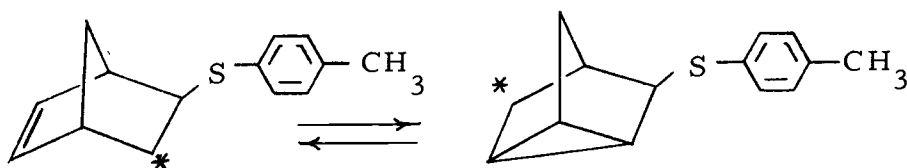
(b) reaction via a single non-classical radical intermediate.
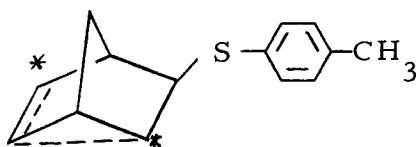
An excellent method to distinguish between these two types of inter-

mediates has been devised by Seubold (54). If the intermediate is a

single non-classical species, then changes in concentration of the

chain transfer agent should not affect the relative proportions of

rearranged and unrearranged products. However, if an equilibrating

pair of classical radicals is implicated, then dilution of the chain

transfer agent should result in a higher ratio of rearranged/unre-

arranged products. Dilution experiments in the above case ruled

out the non-classical radical. Competition experiments showed that

norbornadiene reacted faster than norbornene and cyclohexene. This

was easily explained as due to the greater strain in the starting

norbornadiene than in the other two olefins. Similar conclusions

emerged from a study of the radical addition of benzenesulfonyl chlor-

ide to norbornadiene, carried out by Cristol and Davies (55).

Further endorsement of this picture came from the report of

Trecker and Henry (56) on the free radical addition of chloroform

and carbon tetrachloride to norbornadiene. These additions resulted

in the formation of the nortricyclyl derivative as the sole 1:1 adduct.

Higher telomers were obtained as minor products. The exclusive

formation of the rearranged product was rationalized on the basis
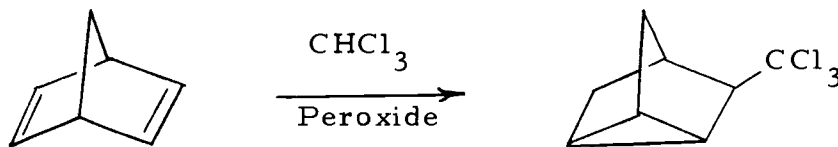
of faster rate of rearrangement relative to chain transfer of the

intermediate adduct radical. Competition experiments showed that

norbornadiene reacted twice as fast as norbornene. This means

that the effect of the second double bond is strictly additive. This
provides a powerful argument against the non-classical radical.

A host of reports pointing to similar conclusions appeared
subsequently. The photoreaction of norbornene with t-butyl hypo-
chlorite, studied by Toebler and his co-workers (57) is interesting
in that both addition and substitution occur, addition predominating.
The results are as follows.

t-BuOCl
→
t-BuOH
hν
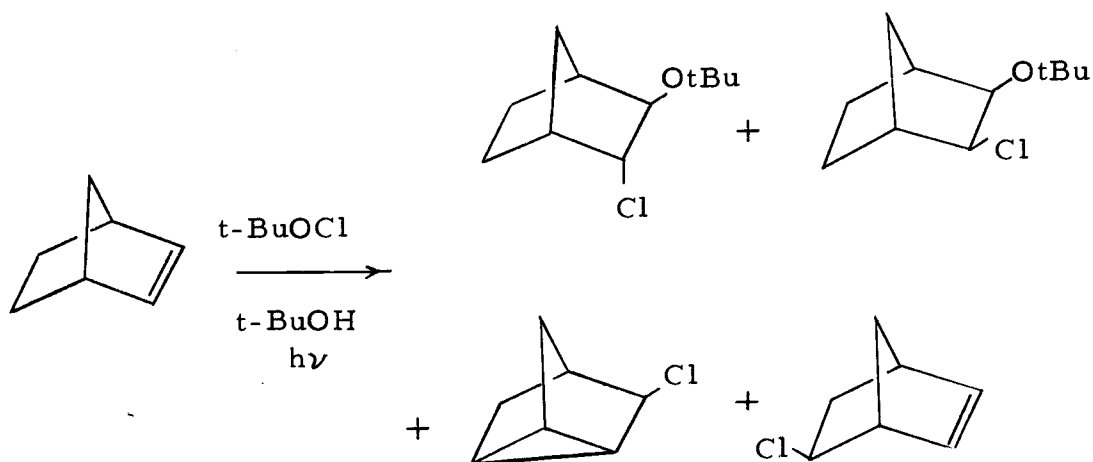
The <u>trans</u>- and the <u>cis</u>-adducts are in the ratio 4:1. The predom-
inance of the <u>trans</u>-adduct would rule out the non-classical 2-norbornyl
radical. The formation of some <u>cis</u>-adduct is readily understandable
in view of the fact that the t-butoxy group causes less effective steric
blocking of the <u>exo</u>-side than the trichloromethyl or the p-tosyl group.
Dilution experiments in the same reaction performed by Poutsma
(58) afforded convincing evidence against the non-classical 5-norbornenyl
radical, arising from hydrogen abstraction.

An ingenious method was used by Kuivila and his co-workers

(59) to generate the 5-norbornenyl and nortricyclyl radicals. Radical reduction of 5-norbornenyl and nortricyclyl chlorides or bromides with tri-n-butyltin hydride yielded the same mixture of norbornene and nortricyclene (in roughly equal amounts). In the neat reaction with nortricyclyl bromide, nortricyclene was formed in greater
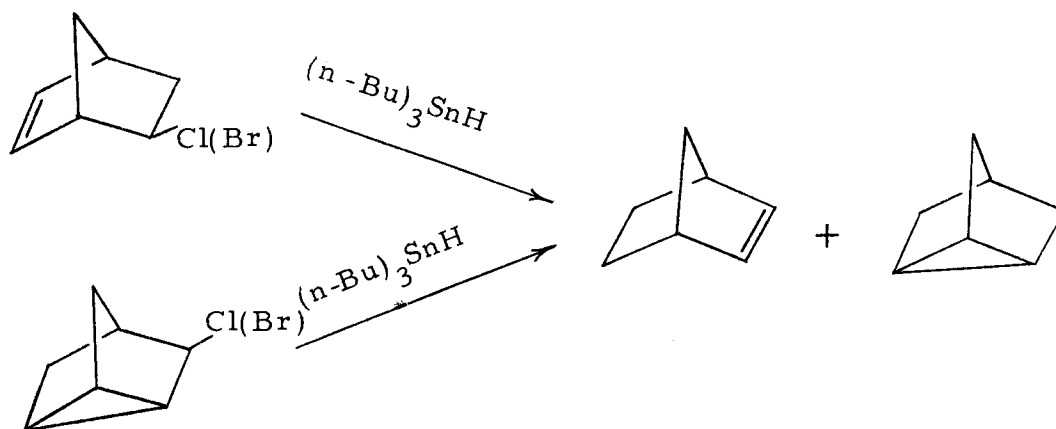
amount and in pentane, norbornene predominated. Thus some of the nortricyclyl radical was trapped before equilibration with the norbornenyl radical. This observation argued against the non-classical radical.

A similar verdict awaited the 7-norbornenyl radical also. Molecular orbital calculations suggested that this radical should be delocalized (60) but experimental results run counter to this prediction. Wilt and Levin (61) observed that decarbonylation of anti-7-norbornene carboxaldehyde was faster than that of endo-5-norbornene carboxaldehyde, possibly due to anchimeric assistance to the loss of carbon monoxide by the π-electrons in the former.
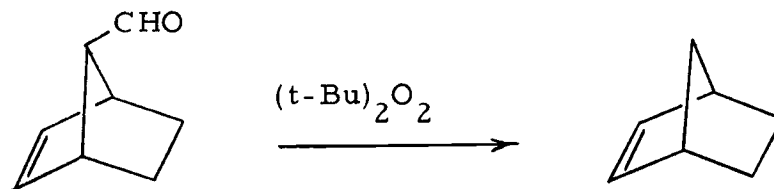
Later, Warkentin and Sanford (62) reported that the radical

reduction of syn- and anti-7-bromonorbornene with tri-n-butyltin

deuteride yielded exclusively anti-7-deuterionorbornene. This

stereochemical result was attributed by the authors to the interven-

tion of the delocalized radical 50. However, this report proved to

50
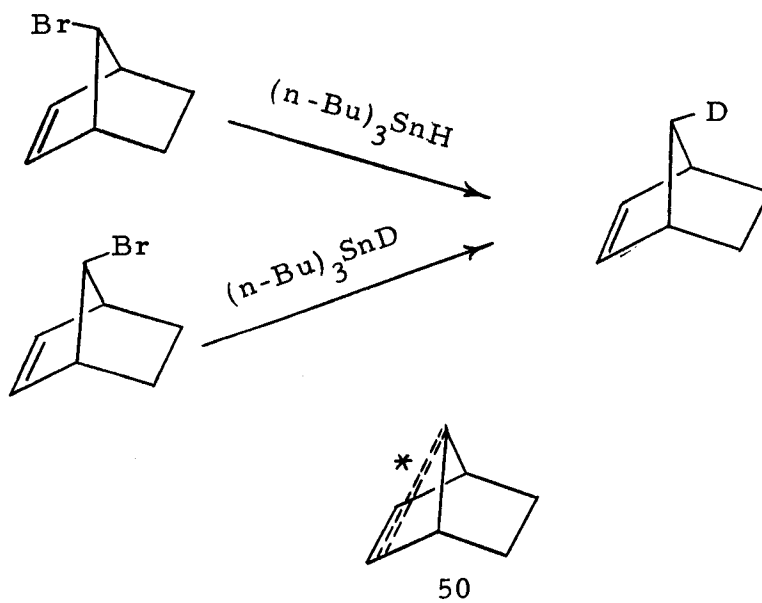
be incorrect as demonstrated by Cristol and Noreen (63) who showed

that Warkentin and Sanford had actually a 70:30 mixture of anti- and

syn-7-deuterionorbornene, thus virtually precluding any need to

invoke the non-classical radical. Cristol and Noreen also observed

that reduction of both syn- and anti-7-bromobenzonorbornadine with

tri-n-butyltin deuteride resulted in identical mixtures of syn- and

anti-7-deuteriobenzonorbornadiene in the ratio 57:43±3. This result

again shows that there is no need to postulate the existence of non-

classical radical intermediates.

A recent report by Jarvis and Yount (64) on the benzonorbornenyl

system provides experimental evidence against a non-classical rad-

ical intermediate. These workers reduced the trichloride 51 with

tri-n-butyltin hydride and found that the only observable product was

syn-8-chloro-5-chorodibenzobicyclo[3.2.1]octadiene (52), the epimer

whose configuration at C-8 is opposite to that expected if the more

favorably disposed anti-benzene ring had participated in the chain

transfer step. The product could be easily explained entirely in

terms of a classical radical which undergoes chain transfer from

the sterically less hindered anti-side.

Cl Cl

(n-Bu)$_3$SnH

H Cl

<u>51</u>

<u>52</u>

Cl

Cl

Cl

<u>53</u>

Cl H

Cl
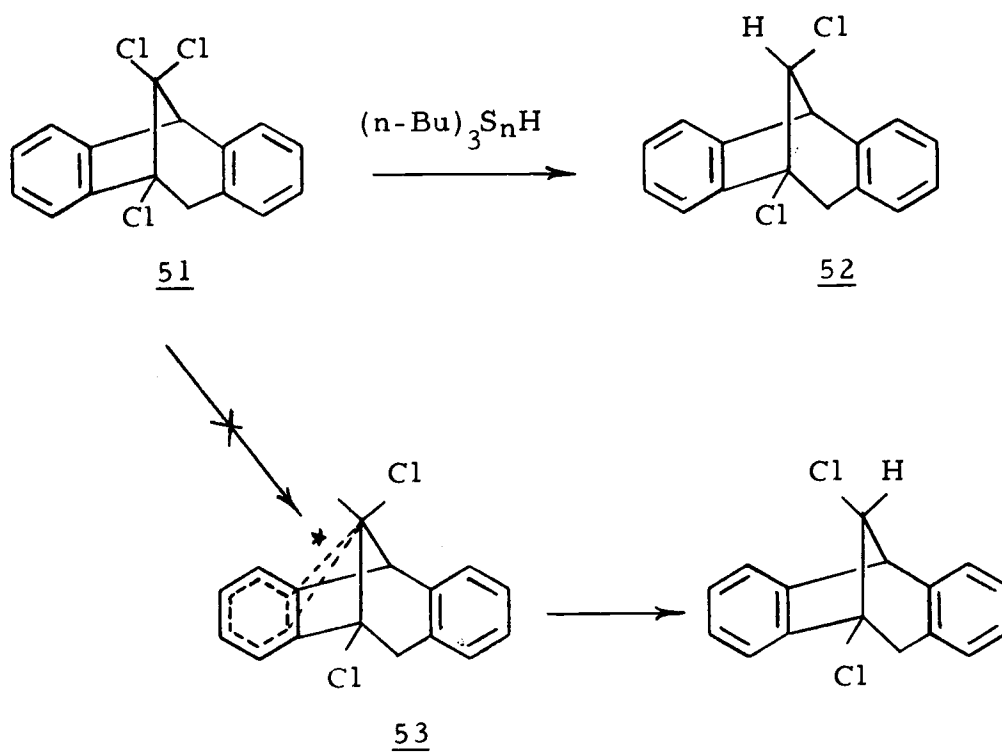
II. RESULTS AND DISCUSSION

Carbene Study

The possibility that non-classical carbenes might exist prompted several workers to engage in studies designed to uncover them, especially in bridged polycyclic systems, but most of their attempts were fruitless, due mainly to the incidence of γ-insertion and/or 1,2-hydrogen migration, two well-known reaction routes of carbenes. The operation of Bredt's rule conferred on exo-8-carbena-tricyclo[3.2.1.0^{2,4}]octane immunity from reacting via a 1,2-hydrogen shift, but nevertheless no cyclopropane interaction with the carbene site was observed, evidently owing to the fact that the p-like orbitals of the exo-cyclopropane ring point down and away from the reactive 8-position (33). We felt that this absence of cyclopropane interaction of the "trishomocyclopropenyl" type in the exo-isomer need not be true of the endo-isomer in which the p-like orbitals of the cyclopropane ring are ideally oriented for overlap with the empty p orbital of the singlet carbene carbon at the 8-position. Actuated by a desire to have a peep into the nature of this divalent intermediate, we embarked on a study of its generation and fate.

At the inception of this study, our task was considerably facilitated by the appearance of several reports of synthetic and/or solvolytic studies in the endo-system (15-17, 65, 66). Benefitting

from these reports, the endo-ketone was prepared using the synthetic

procedure (Scheme I) starting from hexachlorocyclpentadiene 1. The

latter compound was converted to 5,5-dimethoxy tetrachlorocyclo-

pentadiene 2 by treatment with methanolic potassium hydroxide solu-

tion in a yield of 72.6%. Diels-Alder reaction of this diene at 0° with

cyclopropene generated by the method of Closs and Krantz (67) re-

sulted in near-quantitative yield of the adduct ketal 3. Dechlorina-

tion of 3 with lithium, followed by hydrolysis with glacial acetic acid,

gave the saturated ketone 5 in good yield as previously reported. The

ketone was smoothly converted to its tosylhydrazone 6 in 62% yield

by refluxing it in ethanol solution with tosylhydrazine.

The tosylhydrazone was then subjected to methoxide ion-induced

decomposition at 150-155° in anhydrous diglyme using a tosylhyd-

razone-sodium methoxide molar ratio of 1:5.74. Vpc analysis of

the products revealed that the products were composed of four com-

ponents in the ratio 4:33:11:51 in the order of increasing retention

times plus an additional 1% component which was not isolated (yield

ca. 80%). The four products were isolated by vpc collection and

submitted to spectral examination in order to ascertain their struc-

tures.

The 4% component showed characteristic ir bands at 3050 cm^{-1},

assignable to cyclopropyl C-H stretching, 3030 cm^{-1}, attributable

to olefinic C-H stretching, and 1596 cm^{-1}, indicative of the presence

Scheme I
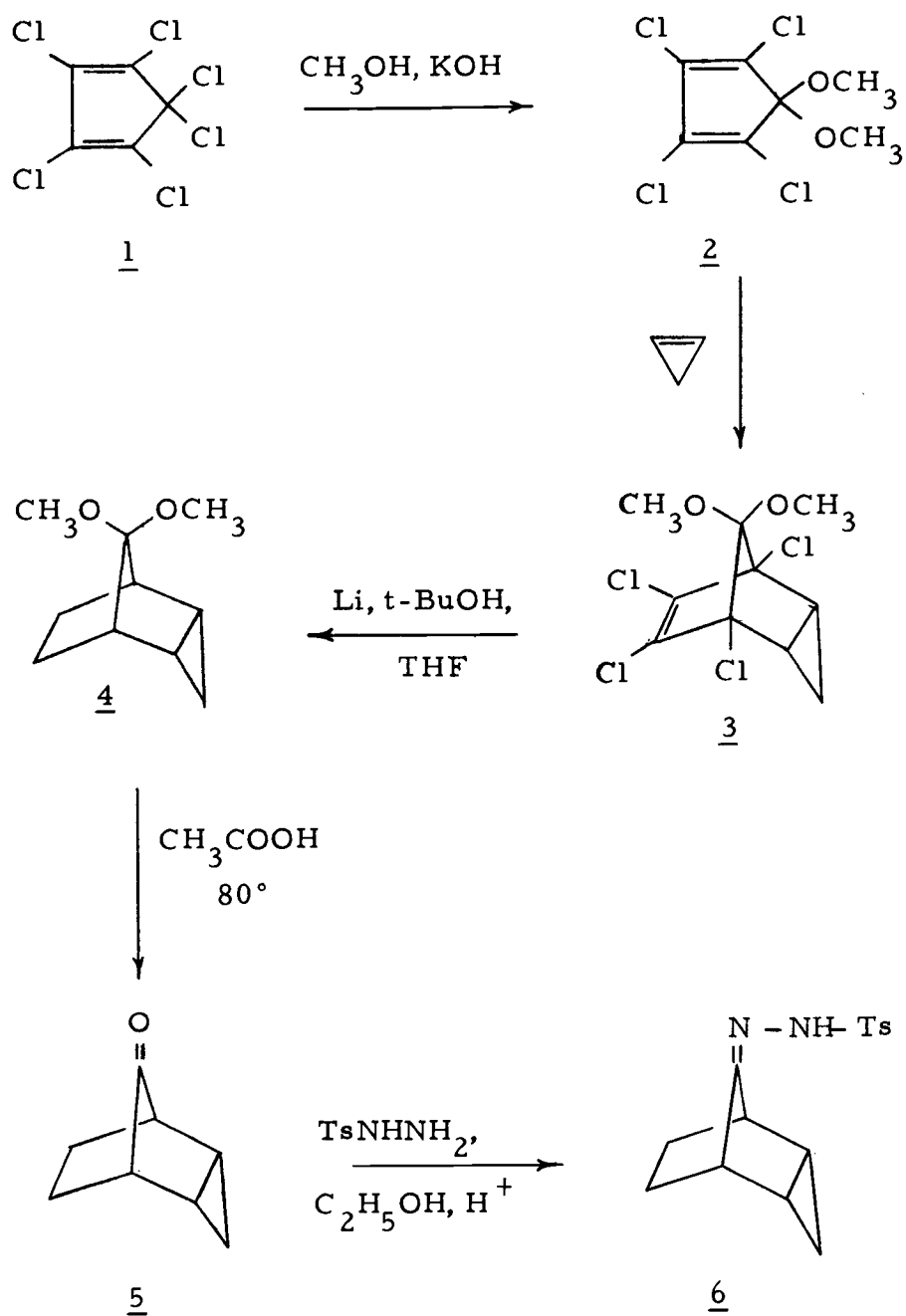
of a C=C bond. Its nmr spectrum (60 MHz, CCl_4) showed signals at

τ4.5-4.8 (doublet of a quartet, 2H, olefinic protons), 6.85-7.1

(multiplet, 1H), 7.4-8.45 (multiplets, 7H). These data are nicely

accommodated by structure 9. It was subsequently learned that 9

was observed as a product of photoisomerization of 1, 3, 5-cyclo-

octatriene by Winstein and Zirner (68) as well as by Roth and Peltzer

(69). Comparison of ir and nmr spectra with those supplied by these

authors revealed that samples of 9 prepared by these two routes

were identical.

The 33% constituent had vpc retention time, ir, nmr, and mass

spectra identical to those of an authentic sample of tetracyclo-

[3.3.0.0^{2,8}0^{4,6}]octane 10, which had previously been obtained by

Freeman, Kuper, and Rao (33, 70) by irradiation of exo or endo-

tricyclo[3.2.1.0^{2,4}]oct-6-ene.
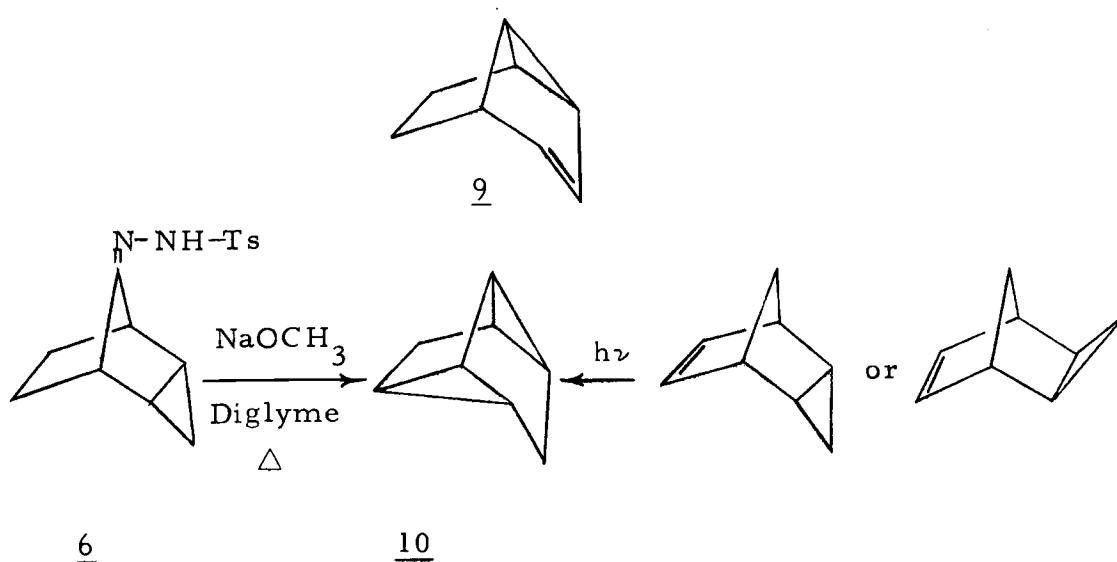
The mass spectrum of the 11% component showed a parent peak of m/e 138 and the ir spectrum exhibited principal bands at 3090, 3030, and 3010 cm^{-1}, all assignable to cyclopropyl C-H stretching, 1195, 1120, and 1100 cm^{-1}, strongly suggestive of ether C-O linkage. Its nmr spectrum (100 MHz, CCl_4) displayed signals at τ6.5 (unresolved triplet, 1H), 6.85 (singlet, 3H), 7.8-8 (multiplet, 2H) and 8.4-9.75 (multiplets, 8H). The triplet at τ6.5 was assigned to the proton α to oxygen and the three-proton singlet at τ6.85 to the methoxy protons. It was clear that the compound was a methyl ether. The upfield signals, extending up to τ9.75 indicated the presence of cyclopropane methylene. It was also found that the hydrocarbon portion of the spectrum was very similar to its counterpart in the case of endo-anti-tricyclo[3.2.1.0^{2,4}]-octan-8-ol (17). On this basis, this component was tentatively identified as anti-8-methoxy-endo-tricyclo[3.2.1.0^{2,4}]octane 11.

Unequivocal proof of this structure stemmed from an independent synthesis. The endo-ketone 5 was reduced with lithium aluminum hydride to a 64:36 mixture of the syn- and anti-alcohols 14. Treatment of this mixture with sodium hydride and methyl iodide gave two isomeric ethers in the ratio 37:63 in the order of increasing retention times. The 37% ether which should be the anti-ether had vpc retention time, ir and nmr spectra identical to those of the 11% component of the tosylhydrazone decomposition products. The 63%

ether which must be the syn-ether 13 had characteristic ir bands at

3095, 3060 and 3030 cm^{-1} (cyclopropyl C-H stretching) and 1209,

1135, and 1107 cm^{-1} (ether C-O linkage). Its nmr spectrum (100

MHz, CCl$_4$) showed signals at τ 6.25 (unresolved triplet, 1H)

6.73 (singlet, 3H), 7.85 (unresolved triplet, 2H) and 8.47-9.2

(multiplets, 8H). The hydrocarbon portion of the spectrum was

very similar to its counterpart in the spectrum of the syn-alcohol

(17). By comparison of retention times, it was found that this ether

was present to the extent of ca. 1% in the tosylhydrazone decomposi-

tion products.

11   13
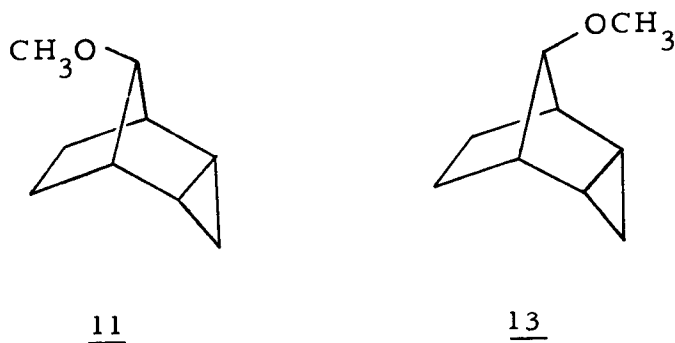
The ir spectrum of the 51% component of the tosylhydrazone

decomposition products displayed strong absorptions at 3035 cm^{-1},

attributable to cyclopropyl C-H stretching, 1115 and 1095 cm^{-1},

strongly suggestive of ether C-O stretching. Its nmr spectrum

(100 MHz, CCl$_4$) showed resonance signals at τ 6.1-6.55 (six-peak

signal, 1H), 6.85 (singlet, 3H), and 7.3-9.1 (multiplets, 10 H).

The signal at τ6.1-6.55 which is assignable to the proton α to oxygen was identical in its splitting pattern to that of the proton α to oxygen in the rearranged endo-alcohol 15 (17) and to that of the α-chloroproton in the rearranged endo-chloride 16 (71). Also the hydrocarbon portion of the spectrum was nearly identical to its counterpart in 15 and 16. On the strength of these data, this component was tentatively identified as endo-2-methoxytricyclo-[3.3.0.0^{4,6}]octane 12.

OH
15

Cl
16
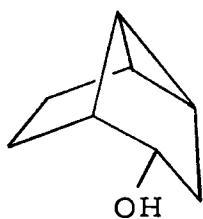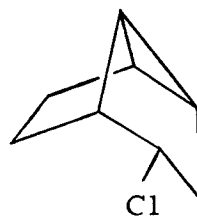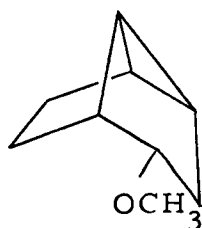
OCH$_3$
12

Confirmation of this structure assignment was sought via an independent synthesis of this ether. Since this carbene work was proceeding concurrently with our study of the photochlorination of exo- and endo-tricyclo[3.2.1.0^{2,4}]octane described later in this chapter, we had on hand a sample of the endo-anti-8-chloride 17.

Since solvolysis of <u>17</u> should give exclusively or predominantly the

rearranged <u>endo</u>-product (14-17), we subjected this chloride to

methanolysis in the presence of calcium carbonate. The sole

product of methanolysis was identical to <u>12</u> as observed by
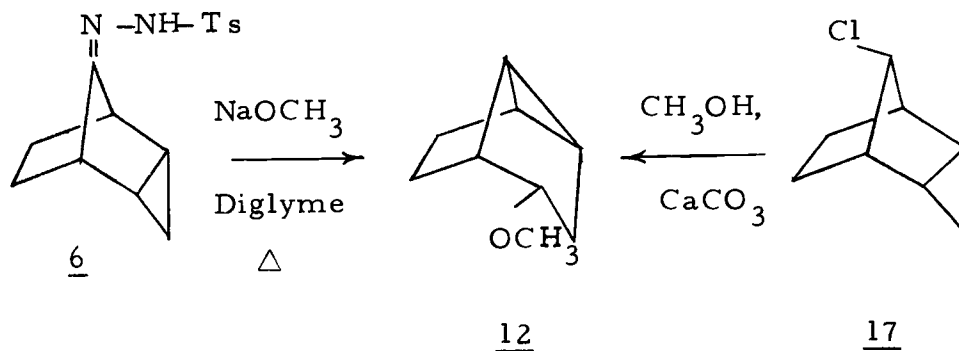
comparison of retention times and ir spectra.

Thus the final results of analysis of the products of the

tosylhydrazone decompostion are as follows:

CH_3O

11 (11%)

+

OCH_3

12 (51%)

OH NaH

CH_3I

OCH_3

Cl

14

13 (1%)

17
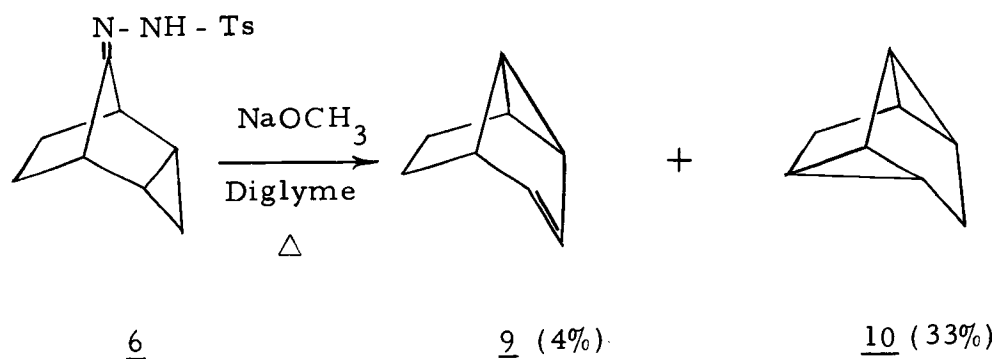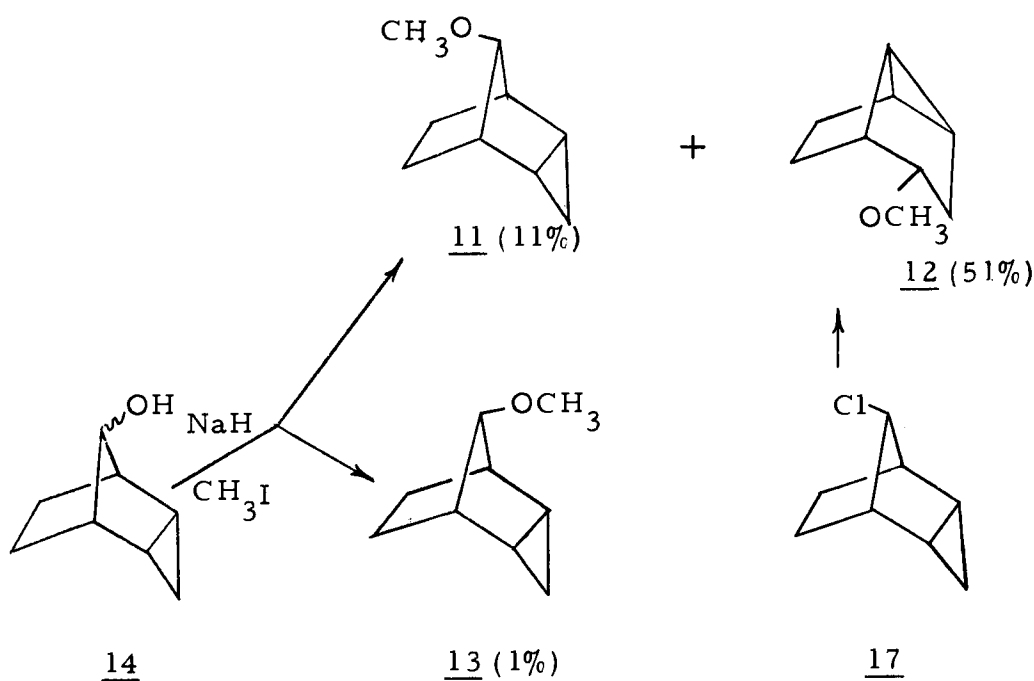
There was a small peak in the hydrocarbon region in vpc, amounting to less than 1% of the products. This peak could not be collected in sufficient quantities for its characterization.

It is logical next to consider the mechanism of the formation of the various products. A detailed study of the base-catalyzed decomposition of tosylhydrazones was recently reported by Shapiro, Duncan, and Clopton (72). These workers investigated in detail the base-induced decomposition of camphor tosylhydrazone and observed (1) that at low concentrations of sodium bases in aprotic solvents, tricyclene 20 appears to be generated from a cationic intermediate; 2) camphene 21 formation is increasingly favored at lower concentrations of sodium bases in aprotic solvents and tricyclene formation
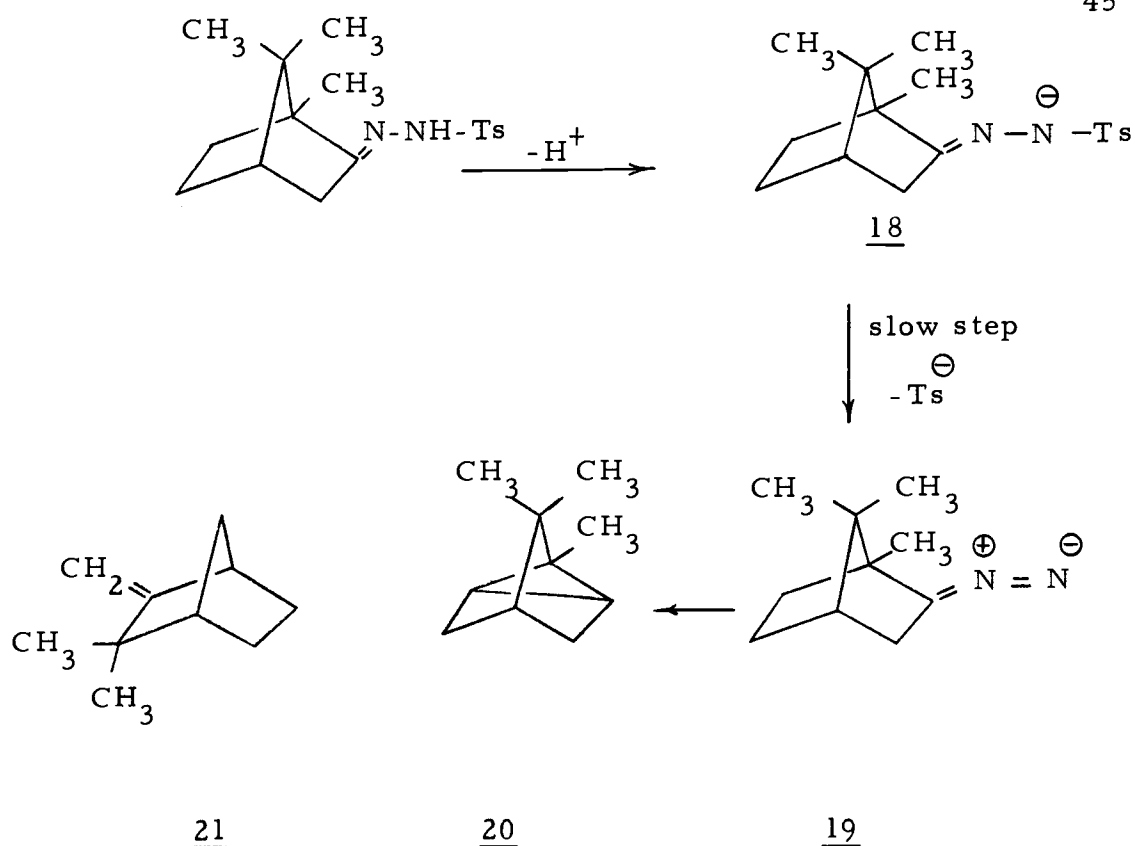
at high base concentration; and 3) camphene formation is favored

in aprotic solvents of higher polarity, other factors being equal.

They also noted that change of base concentration had a more pro-

found effect in determining the tricyclene-camphene ratio than solvent

polarity. The authors propose a mechanism, sketched below (Scheme

II), in which the key step involves the equilibrium between the diazo

compound and its corresponding diazonium cation. In accordance

with the law of mass action, when excess base is used, the equilib-

rium will be shifted in favor of the diazo compound (and hence the

carbene). Under the reaction conditions, both the diazo and diazonium

intermediates can shed nitrogen to give a carbene or carbonium ion,

which lead to products. The diazonium ion can also lead to products

Scheme II

Scheme III

CH$_3$O$^\ominus$ +

$\rightleftharpoons$

+ CH$_3$OH

7a

$\Big\downarrow$ -N$_2$

$\Big\downarrow$ -N$_2$

8

Products

Products

directly.

A piquant situation arises when we apply this scheme to the
present case. Do the methyl ethers arise from the carbene or the
carbonium ion (or diazonium ion) or both? The formation of the
ethers in a stereoselective fashion is seemingly reminiscent of cation
intermediacy. However, since we used a large excess of base and
an aprotic solvent, it would appear that we can assume exclusive
intermediacy of the carbene in the light of Shapiro's scheme. If this
is true, then we have a powerful argument for a non-classical carbene
26, considering the stereospecificity of the products. As carbenes

(in the singlet state) are electrophilic species, it appeared reasonable
to suppose that they might suffer attack by nucleophiles like methoxide
ion. Methoxide attack at C-8 from the anti-side would give the

carbanion 24 which can undergo configurational inversion prior to

neutralization, yielding the anti- and the syn-ethers. The rearranged

endo-ether 12 which appeared to be formed in a highly stereoselective

step is also in accord with this picture. Nevertheless, formation

of endo-tricyclooctyl carbonium ion would be expected to be facilitated

by the strain relief provided by protonation of diazo compound 7a.

Thus, we could not rule out the possibility that the ethers might have

arisen from the cation or from both cationic and carbene precursors.

It would be logical to expect that the hydrocarbons are formed prin-

cipally from the carbene which could possibly be a delocalized species.
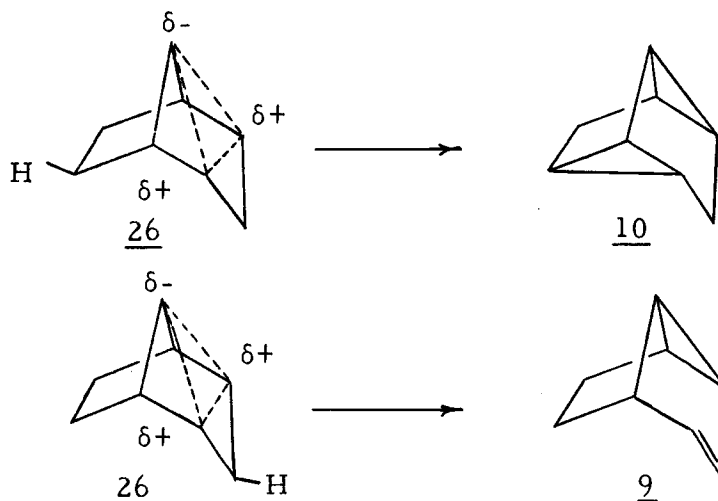
In an effort to separate the carbene from the carbonium ion

components a series of experiments was undertaken. The first was

to study the effect of addition of methanol-O-d to the reaction. The

expectation was, if the ethers arise from the cation, their propor-

tions would increase, relative to the hydrocarbons, since the added

methanol would shift the diazo-diazonium equilibrium to the diazonium

side. Further, the extent of deuteration in the products might offer

some clues regarding the intermediates they arise from. Several

runs were made, holding the concentration of sodium methoxide

virtually constant at 5.75-6.20 equivalents and adding varying amounts

of methanol-O-d. The results are summarized in Table 1.

Table 1. Decomposition of tosylhydrazone $\underline{6}$ at 145-150° in Diglyme/NaOMe/$CH_3OH(D)^d$

Run	(equivalents) $\underline{6}$	$NaOCH_3$ (equivalents)	CH_3OD^c (equivalents)	12^a	$\underline{11}^{a,b}$	$\underline{10}^a$	$\underline{9}^a$
1	1	5.74	0	51	11	33	4
2	1	5.92	1	64	13	21	2
3	1	5.92	5.13	78	13	9	1
4	1	5.75	11.9	81	11	7	1
5	1	6.20	81.7	81	16	3	0

[a] ± 3%.

[b] The presence of the syn-isomer 13 to the extent of ca. 1% was detected in run 1. In all other runs no attempt was made to detect the presence of this isomer.

[c] 83% methanol-O-d.

[d] No attempt was made to find the yield of the products in runs 2-5.

Due to difficulties encountered in the nmr and mass spectral analysis for deuterium in the products, the extent of deuteration in the products could not be estimated. However, the results seem to clearly indicate that the ethers arise from the cation predominantly, if not exclusively, and the hydrocarbons principally from the carbene. In another series of experiments the tosylhydrazone was decomposed at 140-150°, varying the concentration of sodium methoxide from 3.01 to 18.1 equivalents. In every case the product composition remained the same (within ±3%). It appears that a saturated solution of sodium methoxide in diglyme was formed in each case, thus accounting for the constancy of the product composition.

It may be mentioned that the formation of methyl ethers in the decomposition of tosylhydrazones is unprecedented in bridged poly-cyclic systems. The question hence posed itself: Is this an offspring of the incorporation of the cyclopropane ring in the endo-orientation? To answer this question a knowledge of the results of the base-catalyzed decomposition of norbornan-7-one tosylhydrazone was needed. Since the report by Moss (24) on 7-carbenanorbornane was based on the results of the pyrolysis of the dry lithium salt, it could not throw any light on this aspect of the problem. Therefore, we reinvestigated this process under our reaction conditions. Vpc analysis showed that the products were composed of 51% of 7-meth-oxynorbornane 27 and 49% of three hydrocarbons (in the proportions

6, 38 and 4% in order of increasing retention times) in an overall

yield of 97%. The identity of the methyl ether was unequivocally

established by comparison of its vpc retention time and ir spectrum

with those of an authentic sample synthesized by treatment of

7-hydroxynorbornane with sodium hydride and methyl iodide. The
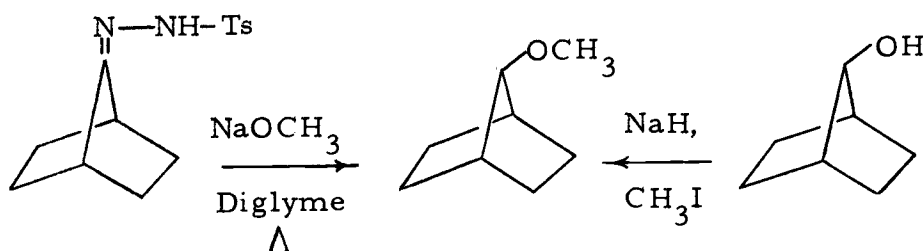
27

hydrocarbon products were not analyzed. From this it can be

gathered that methyl ether formation is not due to the influence of

the cyclopropane ring but can be traced principally to an enhanced

formation of diazonium ion due to relief of strain.

At this point the following question was faced: Is the carbene

the exclusive intermediate leading to the hydrocarbon products? We

sought a decisive verdict on this problem via the decomposition of

the tosylhydrazone-N-d, 28. The idea was that since methanol-O-d

would be the result of neutralization of 28 by methoxide, the resulting

isotope effect on the conversion of the diazo compound to the dia-

zonium cation would decelerate the formation of carbonium ion

products and thereby promote carbene-forming conditions.

After some initial difficulties, essentially complete ($\geq$97%)

deuteration was accomplished by repeated treatment of a suspension

of the tosylhydrazone in methylene chloride with D_2O and a few drops

of Aliquat 336 (methyl tricaprylyl ammonium chloride) (73).

Vpc analysis of the products of the decomposition of the deuter-

ated tosylhydrazone under the usual conditions revealed a dramatic

and stunning change in the composition of the products. The hydro-

carbons comprised 91% of the products, the ethers accounting for

the remainder. The results were as follows:

N—ND—Ts

CH₃O

NaOCH₃
───────→
Diglyme
Δ

OCH₃

+ + +

28

12

6%

11

3%

10

81%

9

10%
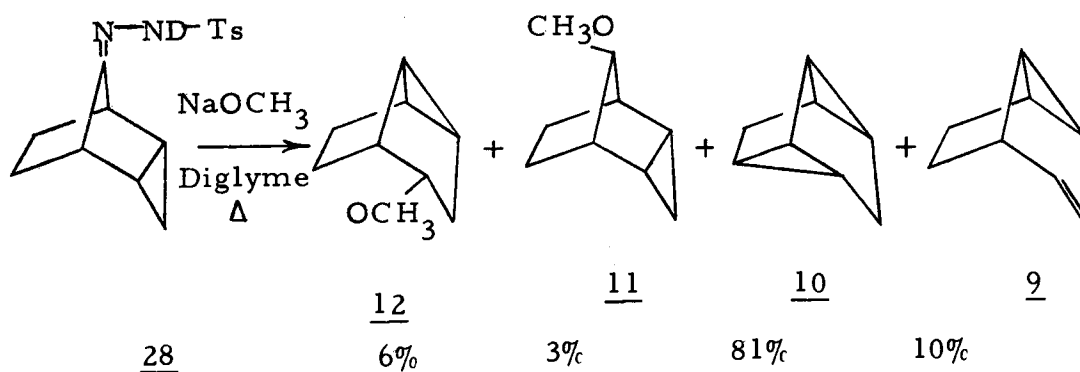
The anticipated isotope effect had clearly materialized. There was

no doubt now that the ethers arise from the cation and the hydro-

carbons from the carbene. Similar isotope effects have been noted

by Wiberg and Lavanish (74) and Schechter and his co-workers (75,

76). These workers found that in the base-catalyzed decomposition

of cyclopropanecarboxaldehyde tosylhydrazone, the principal products

were bicyclobutane and cyclobutene. When an aprotic solvent and

an excess of base were used, cyclobutene was the major product;
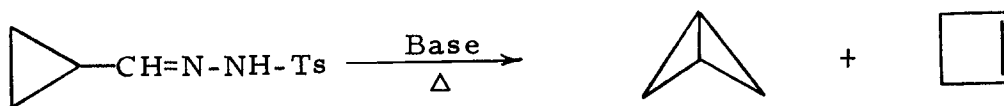
when a protic solvent or insufficient amount of base was used,

bicyclobutane predominated. These are consistent with a cationic

precursor for bicyclobutane and a carbene precursor for cyclobutene.

Furthermore, the formation of cyclobutene was favored over bicyclo-

butane when the tosylhydrazone was decomposed in ethylene glycol-d$_2$

rather than in protoethylene glycol, thus strengthening the above

inference.

Returning to the mode of formation of the hydrocarbons from

the carbene, it is clear that the carbene intermediate rearranges

with transannular trishomocyclopropenyl participation. Representing

the intermediate as 26, loss of a proton from C-6 would yield 10

while loss of a proton from C-3 would lead to the olefin 9. Two

26

Pathway A
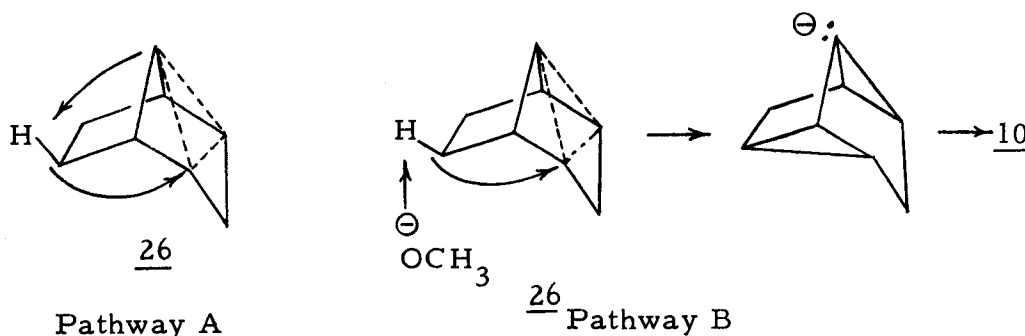
26 Pathway B

possible pathways could be envisioned for the formation of the tetra-

cyclic hydrocarbon 10, a concerted pathway (pathway A) and a

stepwise anionic pathway (pathway B). Pathway A, representing the

carbene as a delocalized species, involves concerted breakage of

C_2-C_4 bond, C_2-C_8 bond formation, hydrogen migration from C_6 to

C_8 and bond formation between C_6 and C_4. This could be described as

$\sigma^2 a + \omega^o a \not\downarrow \omega^2 a$ process which is symmetry-allowed thermally by the

Woodward-Hoffmann rules for pericyclic reactions (77). This con-

certed pathway would require that the tetracyclic hydrocarbon from

the decomposition of tosylhydrazone-N-d, 28 be completely free of

the deuterium label. On the contrary, pathway B involves the forma-

tion of a carbanion which then undergoes protonation. Wiberg (78)

has observed that the neutralization of carbanions exhibits a deuter-

ium isotope effect near unity for deuterium incorporation. On this

basis, operation of pathway B would be expected to lead to tetracyclic

hydrocarbon 10 almost completely deuterated ($\geq 97\%$ d_1) as the only

source of protons (or deuterons) is the methanol-O-d of neutraliza-

tion. Mass spectral analysis of the tetracyclic hydrocarbon revealed

that it had 23 (± 3)% d_1. The possibility that this deuterium in the

hydrocarbon could have arisen partly or completely from a base-

catalyzed exchange of the tetracyclic hydrocarbon subsequent to its

formation could be ruled out as it failed to undergo any detectable

exchange when a pure sample of the undeuterated hydrocarbon was

submitted to the reaction conditions. The fact emerges therefore

that the concerted process from the delocalized carbene is the major

pathway with the anionic pathway being possibly the minor route to

the tetracyclic hydrocarbon.

Summing up, the similarity of the behavior of the carbene to its

cationic analog is amply evidenced by its display of transannular

trishomocyclopropenyl participation. This is in distinct contrast

to the case of the exo-isomer whose behavior has been rationalized

as proceeding via a 1, 2-alkyl shift. It is also noteworthy that the

carbene appears to be in the singlet state. Pertinently, we have not

observed any radical-like behavior, like hydrogen abstraction, which

would be expected of a triplet carbene. Therefore, we suggest that

the transition state for hydrogen migration in the carbene involves

non-classical delocalization, and it seems likely that the intermed-

iate is also non-classical. Whether the latter is true or not and the

chemical significance of such delocalization are matters to be deter-

mined by additional experimentation.

Free Radical Study

Concurrently with our carbene study, an investigation of the

free radical abstraction patterns for exo- and endo-tricyclo-

[3. 2. 1. 0$^{2, 4}$]octane was undertaken. This work had its genesis in

the thesis research of Fenwick (79). Fenwick reported that the free

radical chlorination of exo-tricyclo[3. 2. 1. 0$^{2, 4}$]octane, 29 gave the

exo-6-chloride 30 (91.8%), the anti-8-chloride 31 (6. 3%) and the

anti-3-chloride 32 (1.8%) in a total yield of 43.5%. The completely

stereospecific formation of the exo-6-chloride provides a powerful

argument for the intervention of a non-classical radical. This result

is in sharp contrast to the results reported for the norbornyl system

(see Chapter I). The reported formation of the anti-3-chloride 32

is rather surprising in view of the earlier report of Freeman and

| 29 | 30 | 31 | 32 |
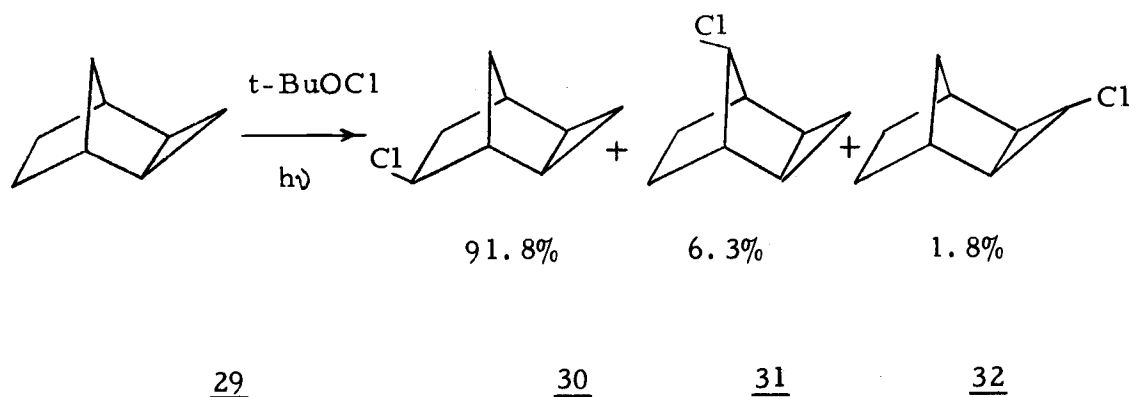
his co-workers (44) on the radical chlorination of bicyclo[3.1.0]-

hexane in which no abstraction of cyclopropane hydrogen atoms was

observed. In fact comparison of the nmr spectrum reported by

Fenwick for 32 with that of an authentic sample of this compound

supplied by Professor Jefford (80, 81) revealed that the two samples

were poles asunder in their spectral characteristics. Also the nmr

spectrum reported by Fenwick as that of the anti-8-chloride 31

seemed to be incompatible with this structure.

Another major observation reported by Fenwick was that the

radical chlorination of the endo-hydrocarbon 33 gave exclusively the

anti-8-chloride <u>17</u>, basing his structure assignment on spectral and kinetic data. He proposed that a delocalized radical <u>34</u> intervened and gave <u>17</u> in a stereospecific fashion.

t-BuOCl

CCl_4

hν

<u>33</u>

Cl

<u>17</u>

*

<u>34</u>
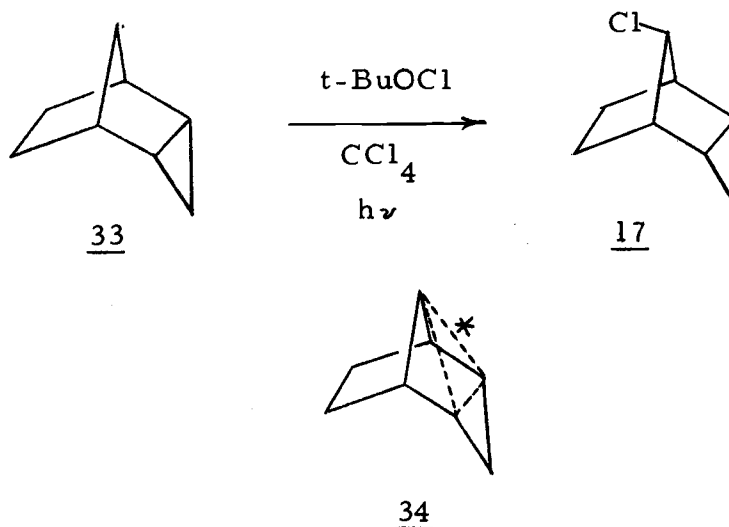
This stereospecific reaction of the radical was surprising in view of numerous earlier reports to the contrary in the norbornyl system (see Chapter I). The suggestion of a non-classical radical runs counter to the general consensus among workers in free radical chemistry, viz., that the reactions of radicals could be explained satisfactorily in terms of steric factors without having to invoke non-classical radicals.

In view of the aforementioned serious uncertainties, we felt that the photochlorination of the <u>exo</u>- and <u>endo</u>-hydrocarbons should be reinvestigated. The <u>exo</u>-hydrocarbon was obtained by addition of methylene to norbornene according to the Simmons-Smith procedure (82). The <u>endo</u>-hydrocarbon was prepared by catalytic

hydrogenation of endo-tricyclo$[3.2.1\ 0^{2,4}]$oct-6-ene, synthesized

by the Diels-Alder addition of cyclopropene to cyclopentadiene

according to the method of Closs and Krantz (67).

Photochlorination of the hydrocarbons was accomplished by

irradiating a mixture of the appropriate hydrocarbon and t-butyl-

hypochlorite in carbon tetrachloride solution at 40° --a procedure

similar to that of Walling and Jacknow in their pioneering studies

(83). A radical chain mechanism has been established by these

authors for the chlorination of hydrocarbons with t-butylhypochlorite.

$$\text{t-BuOCl} \xrightarrow[\text{or}\ \Delta]{\text{h}\nu} \text{t-BuO·} + \text{Cl·}$$

$$\text{t-BuO·} + \text{R-H} \longrightarrow \text{R·} + \text{t-BuOH}$$

$$\text{R·} + \text{t-BuOCl} \longrightarrow \text{R-Cl} + \text{t-BuO·}$$
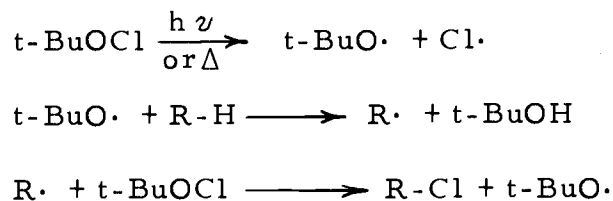
Subjection of the exo-hydrocarbon to photochlorination with

t-butylhypochlorite using a 2:1 molar ratio of hydrocarbon to t-butyl-

hypochlorite, followed by vpc analysis, revealed the presence of

four components in the monochloro region in the ratio 4:17:67:12 in

the order of increasing retention times in a total yield of 27%. No

dichlorides were present--a result brought about by the use of an

excess of hydrocarbon relative to the chlorinating agent. The 4%

component was not isolable in sufficient quantities to enable its

characterization. The other three components were isolated by

vpc collection and each of them on reinjection showed only one peak,

thus testifying to their stability to interconversion on the column

under the conditions of analysis.

The next step was to divest the chlorides of the chloro substitu-

ent and lay bare their basic skeletal pattern. We employed the

elegant method of Kuivila and Beumel (84) to realize this objective.

These authors observed that tri-n-butyltin hydride (TBTH), in the

presence of a suitable radical initiator, abstracts halogen from

alkyl halides, generating the alkyl radical which then abstracts a

hydrogen atom from the hydride to form the alkane.

$$I_N \longrightarrow I\cdot$$
(Initiator)

$$I\cdot + (C_4H_9)_3SnH \longrightarrow (C_4H_9)_3Sn\cdot + IH$$

$$(C_4H_9)_3Sn\cdot + R\text{-}Cl \longrightarrow (C_4H_9)_3SnCl + R\cdot$$

$$R\cdot + (C_4H_9)_3SnH \longrightarrow RH + (C_4H_9)_3Sn\cdot$$
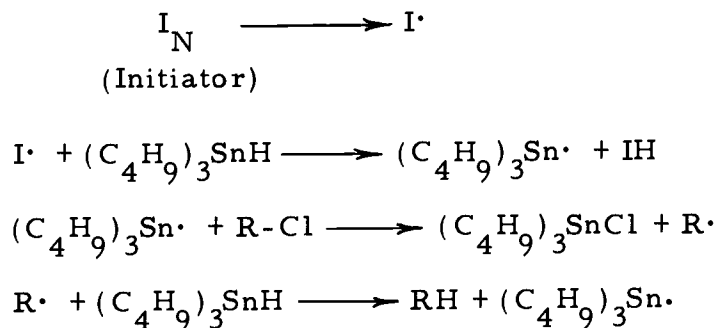
The advantage of this method is that it enables us to detect any re-

arrangement of the radical generated by the action of the t-butoxy

radical since a reversal of this rearrangement would be expected to

be energetically prohibitive. Accordingly the mixture of chlorides

was reduced with TBTH at 95±2° using azobisisobutyronitrile (AIBN)

as the initiator. Vpc analysis showed the presence of only one

hydrocarbon in a yield of 60% (versus cyclohexane internal standard).

The solitary hydrocarbon product was identified as exo-tricyclo-

[3.2.1.0^{2,4}]octane, 29 by comparison of its vpc retention time, ir,

and nmr spectra with those of an authentic sample. The presence

of this ring system in all the chloride products was hence established
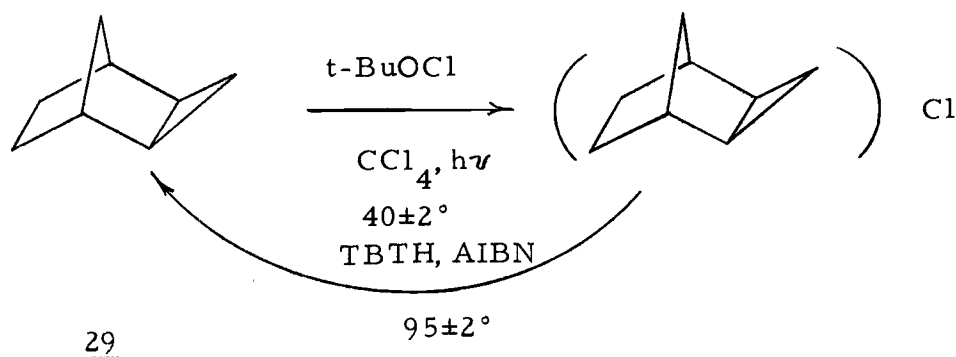
and further confirmation was to follow from detailed spectral exami-

nation of the individual chlorides.

The 67% component exhibited principal bands in its ir spectrum

at 3080 and 3020 cm^{-1}, both assignable to cyclopropyl C-H stretching,

1010 cm^{-1} assignable to cyclopropyl ring deformation, and 750 and

733 cm^{-1}, both assignable to C-Cl stretching. Its nmr spectrum

(100 MHz, CCl$_4$) showed resonance signals at τ6.45 (triplet of a

doublet, J = 6.5 Hz, 2.0 Hz, 1H), 7.6 (envelope, 1H), 7.75 (poorly

resolved multiplet, 1H), 8.05 (a series of four doublets, J = 13 Hz.,

6.5 Hz, 2.5 Hz, 1Hz), 8.3 (triplet of a doublet, J = 13 Hz, 3.5 Hz, 1H), 8.8

(doublet, J = 10.5 Hz, 1H), 9.1 (multiplet of a doublet, J = 10.5 Hz,

1H), 9.45 (a complex multiplet, 3H), and 9.9 (multiplet, 1H). The

signal at τ6.45 which is assignable to the α-chloroproton was identi-

cal in its splitting pattern to that of the α-hydroxy proton in the

spectrum of exo-6-hydroxy-exo-tricyclo[3.2.1.0^{2,4}]octane. The

hydrocarbon portion of the chloride spectrum was also very similar

to that of this alcohol. On this basis, this chloride was tentatively

assigned the structure exo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane,

30 and the resonance signals assigned as shown. The signal at τ 8.05

is interpretable as an AB pattern of a doublet (J=13 Hz) each line of

which is split twice into a doublet (J=7 Hz, J = 2 Hz) and is assigned

to endo-C_7 proton on the basis of expected coupling of this proton

with the exo-C_7 proton (J=13 Hz), the endo-C_6 proton (J=7 Hz) and

the syn-C_8 proton (J=2 Hz). The signal at 8.3 is assigned to the exo-

C_7 proton which is split into a doublet by the endo-C_7 proton (J=13 Hz),

each line of which is split into a triplet by the endo-C_6 proton and the

bridgehead C_1 proton (J=3.5 Hz). The signals at 8.8 and 9.1 are

assignable to the anti-C_8 and the syn-C_8 protons respectively. The

three-proton signal at 9.45 is assigned to the C_2 and C_4 protons and

the syn-C_3 proton on the basis of expected deshielding of the latter

due to steric congestion with the opposed transannular syn-C_8 proton

(85). The mass spectrum of this chloride showed parent peaks at

m/e 142 and 144 as expected.
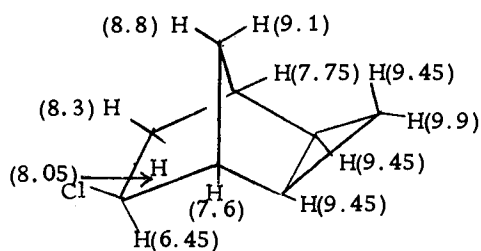
30
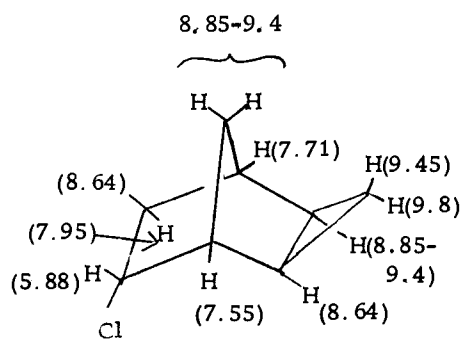
31

The mass spectrum of the 12% component had parent peaks at

m/e 142 and 144. Its ir spectrum showed the absence of unsatura-

tion (no absorption in the region 1500-1700 cm^{-1}), presence of

cyclopropane ring (absorptions at 3105, 3040 and 1034 cm^{-1}) and

the presence of C-Cl bond (absorptions at 757 and 732 cm^{-1}). Its

nmr spectrum (100 MHz, CCl_4) had resonance signals at τ5.88 (trip-

let of a doublet, J = 9 Hz, 3.5 Hz, 1H), 7.55 (unresolved multiplet,

1H), 7.71 (envelope, 1H), 7.95 (multiplet, 1H), 8.64 (multiplet, 2H),

8.85-9.4 (multiplets, 3H), 9.6 (overlapping pair of triplets, J = 3 Hz,

1H) and 9.94 (quartet, J = 7 Hz, 1H). The signal at τ5.88, attribut-

able to the α-chloroproton, was identical in its splitting pattern to

that of the α-hydroxyl proton in the spectrum of endo-6-hydroxy-exo-

tricyclo[3.2.1.0^{2,4}]octane. Indeed the hydrocarbon portions of the

spectra of the chloride and the alcohol were strikingly similar. On

the strength of these data, the chloride in question was tentatively

identified as endo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane 35 with

the spectral signals assigned as shown.

Confirmation of the structure assignments for the two epimeric

chlorides was obtained by independent syntheses of the chlorides.

Addition of hydrogen chloride to exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene

in methylene chloride gave two monochlorides in the ratio 48:52.

The 52% component was identical to the major monochloro product

of the photochlorination reaction. The 48% fraction was an olefinic

chloride and therefore was not characterized completely.

$$\underline{29} \qquad\qquad \underline{30}$$
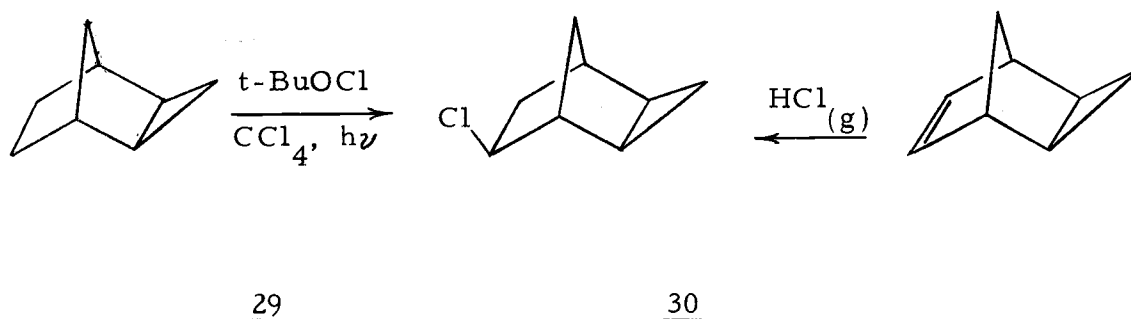
The <u>endo</u>-6-chloride <u>35</u> was synthesized using the method of

Weiss and Snyder (86-88) who have found that the reaction of alcohols with

triphenylphosphine and carbon tetrachloride results in the formation

of alkyl chlorides with a predominant or significant tendency for inver-

sion and lack of rearrangement, even in cases where unimolecular

solvolytic displacements lead to products with retention of configura-

tion and/or extensive rearrangement.

$$R_3P: \; + \; Cl\text{-}CCl_3 \longrightarrow R_3PCl^+CCl_3^-$$

$$R_3PCl^+CCl_3^- + R'\text{-}OH \longrightarrow R_3PCl^+OR' + CHCl_3$$

$$R_3PCl^+OR'^- \longrightarrow R_3POR'^+Cl^- \longrightarrow R_3P{=}O + R'Cl$$
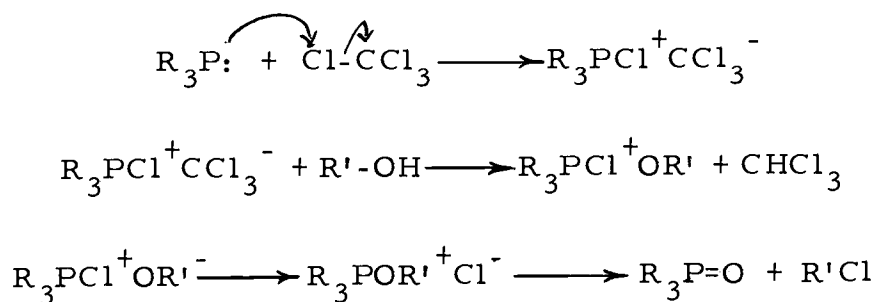
When <u>exo</u>-6-hydroxy-<u>exo</u>-tricyclo[3.2.1.0^{2,4}]octane was stirred with

triphenylphosphine and carbon tetrachloride at room temperature for

24 hr followed by removal of solvent at reduced pressure and pyroly-

sis of the resulting phosphorane ester at 90-130°, the products on

vpc analysis were found to consist of four components in the ratio

3:15:64:18 in the order of increasing retention times in a total yield

of 31%. The 3% component was not isolable in sufficient quantities

to permit its characterization. The 64% and 18% components were

the exo- (30) and endo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (35)

and were identical, respectively to the 67% and 12% components of

the photochlorination products. The 15% component was identified as

nortricyclylmethyl chloride 36 on the basis of its mass spectrum

(parent peaks at m/e = 142 and 144), ir spectrum [strong bands at

3080 cm^{-1} (cyclopropyl C-H stretching), 800 cm^{-1}, characteristic

of the nortricyclene ring and 730 cm^{-1} (C-Cl stretching)], and nmr

spectrum (100 MHz, CCl_4, complex multiplet of two α-chloro protons

at τ6.74, an unresolved one-proton multiplet at τ8.05, a one-proton

multiplet at τ 8.10 and complex multiplets between τ8.5 and 9.5

integrating to 7 protons). The endo-chloride 35 should have arisen

| 37 | 30 | 35 | 36 |
| | (64%) | (18%) | (15%) |
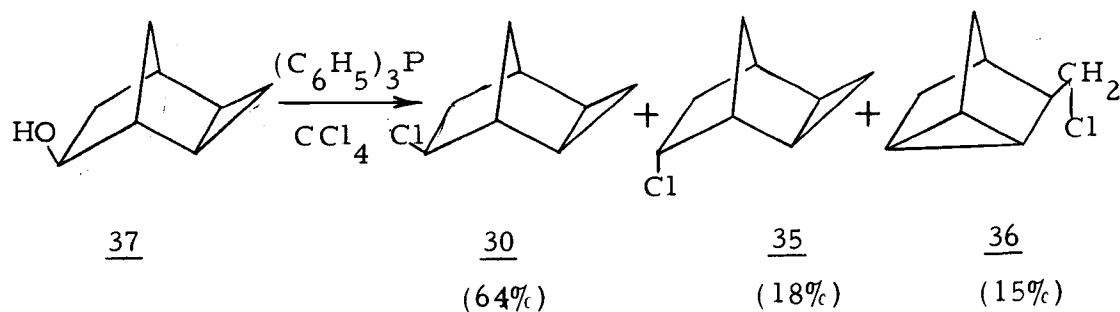
from the expected inversion pathway while the other two chlorides

from the carbonium ion or ion pair pathway. The mechanism of this

reaction will be further commented upon later in this chapter.

The 17% component of the photochlorination products showed

parent peaks at m/e 142 and 144 in its mass spectrum and its ir

spectrum (Figure 7) showed significant bands at 3100, 3030 and

1035 cm^{-1} (cyclopropane ring) and 733 cm^{-1} (C-Cl stretching). There

was a complete absence of bands in the 1500-1700 cm^{-1} region, indi-

cating the absence of C=C double bond. The nmr spectrum (Figure 8)

(100 MHz, CCl$_4$) showed an unresolved one-proton multiplet at τ7.84,

complex overlapping multiplets between 8.1 and 8.60 intergrating to

4 protons, a one-proton doublet of the AB type at 8.67 (J=11 Hz.),

each line being split further into a doublet (J=1.5 Hz.), another such

one-proton doublet at 8.89, complex multiplets at 8.9-9.24 integrating

to two protons, a one-proton five-peak signal at τ9.37 with a spacing

3 Hz between the peaks and a one-proton four-peak signal at 9.87

with a spacing of 7 Hz between the peaks. The two highest field

signals were identical in the splitting patterns to the two highest

field signals in the spectra of the exo-6 chloride 30 and the exo-6-ol

37. These are generally assigned to the syn-C$_3$ and anti-C$_3$ protons

respectively in this system. It seemed clear then that these hydro-

gens did not suffer abstraction. Further, the spectrum was com-

pletely different from that of the anti-3-chloride supplied by Professor

Jefford (80, 81). The syn-3-chloride has been shown to be readily

rearranged to the allylic chloride by these authors. These consider-

ations clearly rule out substitution at C-3 in the present case. As

there is no signal for an α-chloro proton, it is clear that the chloride

is tertiary. Substitution should hence have occurred at C_2 or C_4

or C_1 or C_5. The one-proton five-peak signal at 9.37 which is

assigned to the syn-C_3 proton is interpretable as an overlapping

pair of triplets. A doublet of the AB pattern due to geminal coupling

with the anti-C_3 proton followed by further splitting by two adjacent

protons explains the observed splitting pattern. The four-peak signal

at 9.87 which is assigned to the anti-C_3 proton is similarly explicable

as an overlapping pair of triplets. These splitting patterns require

that the two tertiary cyclopropyl protons on C_2 and C_4 be present

and hence rule out substitution at these two carbon atoms. The only

conclusion possible then is that the chloride in question is 1-chloro-

exo-tricyclo[3. 2. 1. 0$^{2, 4}$]octane, the bridgehead chloride 38, with

the spectral assignment as shown below.

38
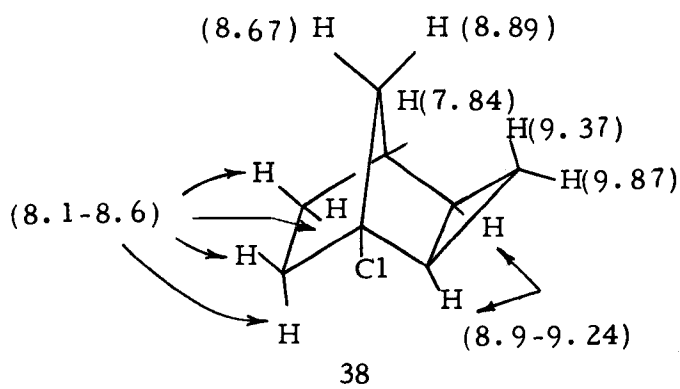
To be entirely certain of the parent ring system, the chloride in

question was reduced with TBTH at 130° with AIBN initiation. The

sole hydrocarbon product was identical to an authentic sample of

<u>exo</u>-tricyclo[3. 2. 1. 0$^{2, 4}$]octane <u>29</u> as observed by comparison of

vpc retention times and mass spectra.

<div align="center">

Cl

<u>38</u>   TBTH, AIBN   →   <u>29</u>

</div>
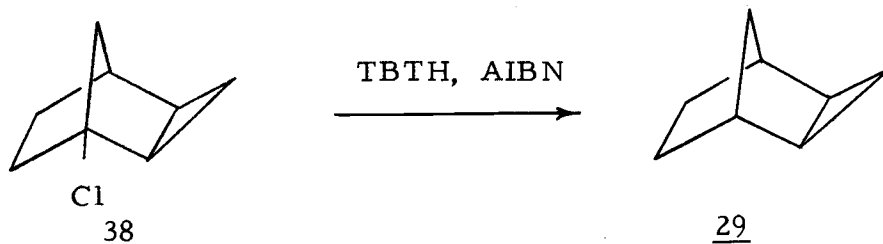
Thus the final results of analysis of the products of photo-

chlorination of the <u>exo</u>-hydrocarbon are as follows:

<div align="center">

<u>29</u>   t-BuOCl / CCl$_4$, hν →   Cl   <u>30</u> / 67%   +   Cl   <u>35</u> / 12%   +   Cl   <u>38</u> / 17%

</div>
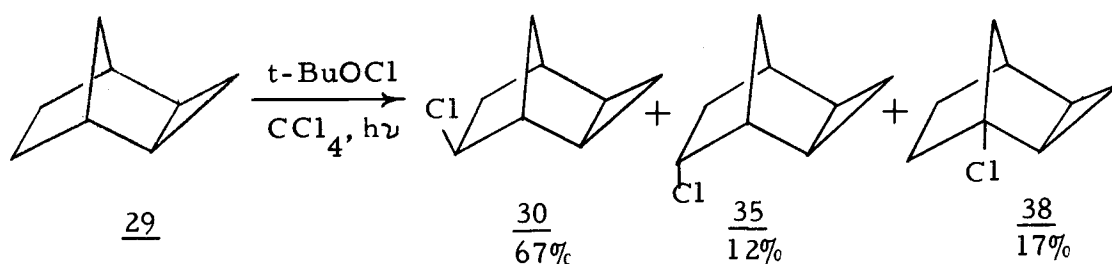
It was also ascertained that the <u>endo</u>-6-chloride <u>35</u> and the bridge-

head chloride <u>38</u> did not result from a secondary reaction of the

<u>exo</u>-6-chloride <u>30</u> as the latter was quite stable to the reaction con-

ditions. Thus we find that hydrogen abstraction occurs to the extent

of 79% at C$_6$ and to a significant extent of 17% at C$_1$. The abstrac-

tion at C$_6$ provides a pattern similar to that found for chlorination

of norbornane with chlorine by Kooyman and Vegter (52). While the

<u>exo</u>/<u>endo</u>-chloride ratio is 67:12 in the present case, it is 70:25 in

the norbornyl case. The smaller proportion of the <u>endo</u>-chloride

in the present case is traceable to the larger size of the chain trans-

fer agent, t-butylhypochlorite, relative to chlorine. Nevertheless,

the absence of fairly complete stereoselectivity in product formation

and the conspicuous lack of skeletal rearrangements make it possible

to rule out any involvement of non-classical radicals of the types <u>39</u>,

<u>40</u>, and <u>41</u> since all these would predict that the substitution at C_6

<u>39</u>   <u>40</u>   <u>41</u>
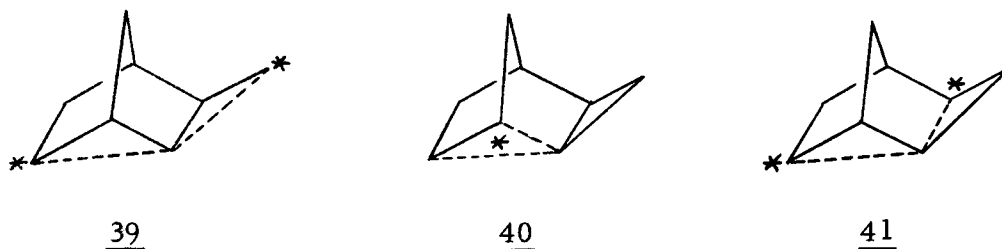
should be completely <u>exo</u>. The products can be accounted for entirely

in terms of a classical radical, the direction of its chain transfer

being controlled by steric factors.

<u>29</u>   t-BuO·   Cl   67%   +   Cl 12%
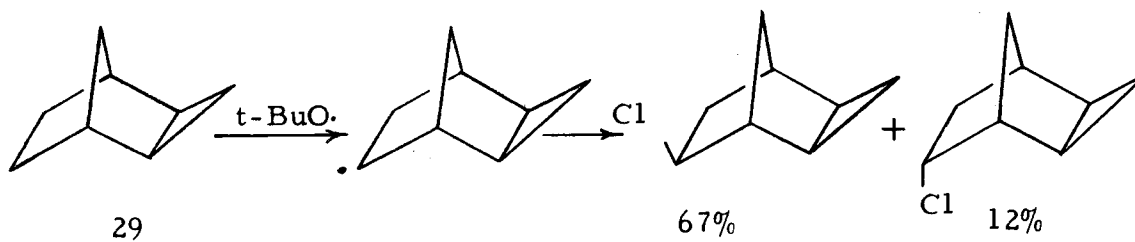
The behavior of the radical is thus in sharp contrast to that of its

cationic analog. Whereas the cation is formed with anchimeric assis-

tance and gives both rearranged and unrearranged products with

essentially complete stereospecificity (89), the radical does not give

rearranged products nor does it undergo stereospecific chain transfer.

The question of anchimeric assistance in radical formation will be

considered later in this chapter.

The formation of the bridgehead chloride to the significant extent

of 17% is rather surprising. Since no hydrogen abstraction was

observed at the bridgehead position in norbornane (52, 90) and

norbornene (57, 58), the incorporation of the cyclopropane ring in

the present case seems to have culminated in some subtle effects

responsible for the observed bridgehead abstraction. The nature

of these forces is presently not clear. Only further work can enlighten

us on this matter.

Having delineated the pattern of radical abstraction in the exo-

system, we switched our attention to the endo-system. Considerable

significance attached to this system in view of its record for solvo-

lytic participation and our study of the divalent carbon intermediate

in this system. The question that was agitating our minds was: will

this system undergo abstraction at the 8-position? Will the radical

intermediate arising therefrom afford evidence of the attributes of

the non-classical species or will it also suffer the fate that overtook

the radicals in the norbornyl system? In any case the results would

have far-reaching implications vis-a-vis the question of non-classical

radical intermediates.

We sought decisive answers to these important questions through

a study of the photochlorination of the endo-hydrocarbon with t-butyl-

hypochlorite. Lest our results should be plagued by significant

amounts of polychlorination, a 2:1 molar ratio of the hydrocarbon

to t-butylhypochlorite was used, as in the case of the exo-isomer.

The analysis of the cohlorination products however confronted us with problems as several chlorides seemed to be present, but eluded satisfactory separation and isolation. Several vpc columns were pressed into service but the problem was never entirely surmounted. The best of the columns tried was 29' column of tris(cyanoethoxy)-propane. It was found subsequently that a combination of vpc and spectral analyses would enable us to estimate the number and the relative proportions of the various products. Resort to this procedure revealed that the photochlorination products consisted of four monochlorides in the ratio of 66:27:5:2 in a yield of 33%. No significant amounts of dichlorides were detectable by vpc. The 2% component was too small to be isolable so that the discussion will be confined to the other three products.

Attention was then focussed on the problem of establishing the identity of each of the three monochlorides. The 66% component showed parent peaks at m/e 142 and 144 in its mass spectrum corresponding to the molecular formula $C_8H_{11}Cl$. The ir spectrum (Figure 9) revealed the absence of C=C double bonds (no absorption in the region 1500-1700 cm^{-1}), the presence of a cyclopropane ring (bands at 3088, 3040, and 3020 cm^{-1} all weak) and the presence of a carbon-chlorine linkage (bands at 785, 760 and 732 cm^{-1}). The nmr spectrum (Figure 10, 100 MHz, CCl_4) showed resonance signals at $\tau 6.28$ (complex multiplet, 1H), 7.63 (unresolved multiplet, 2H), 7.86-8.13 (complex multiplet, 2H), 8.19-8.42 (complex multiplet, 2H),

8.51-8.67 (complex multiplet, 2H) and 9.17-9.37 (complex multiplet,

2H). The compound seemed to have a symmetrical structure. The

hydrocarbon portion of the spectrum was similar to its counterpart

in the spectra of anti-δ-hydroxy-endo-tricyclo[3.2.1.0^{2,4}]octane and

anti-8-methoxy-endo-tricyclo[3.2.1.0^{2,4}]octane. On this basis this

chloride was tentatively identified as anti-8-chloro-endo-tricyclo-

[3.2.1.0^{2,4}]octane 17. The assignment of the spectral signals to

the various protons is shown below. Clinching evidence for this

assignment emerged from the methanolysis of this chloride which

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proceeded stereospecifically to endo-2-methoxy tricyclo[3.3.0.0^{4,6}]-

octane (already referred to in connection with the carbene study).

The 27% component was isolated by repeated vpc collection

and purification and was found to have ir (Figure 11) and nmr spectra

(Figure 12) identical to those of an authentic sample of endo-2-chloro

tricyclo[3.3.0.0^{4,6}]octane 16 supplied by Tanida (71).

The 5% component gave parent peaks at m/e 142 and 144 in its

mass spectrum, corresponding to the formula $C_8H_{11}Cl$. The ir

spectrum (Figure 13) clearly evidenced the presence of a cyclopro-

pane ring and absence of C=C double bonds (absorptions at 3120 (w),

3050 (w) cm^{-1} and no absorption in the region 1500-1700 cm^{-1}). The

presence of C-Cl linkage was indicated by intense bands at 783, 772,

and 725 cm^{-1}. The nmr spectrum (Figure 14, 100 MHz, CCl_4)

exhibited resonance signals at τ 5.95 (triplet of a doublet, J = 11 Hz,

4 Hz, finer splitting of each of the lines to about 1 Hz was also

observable, 1H), 7.52 (envelope, 1H), 7.8-8.03 (complex multiplet,

2H), 8.05-8.23 (complex multiplet, 2H), 8.28-8.83 (complex multi-

plet, 3H), and 8.88-9.13 (doublet of a quartet, J=6.5 Hz., 2 Hz.,

1H). The signal at 5.95 which is assignable to the α-chloro proton

shows that this proton is coupled to three other protons. This fact,

coupled with the fact that there are at least five unique protons rules

out the syn-chloride 42.

42   43   44

45   46
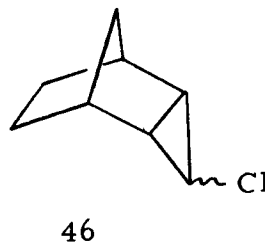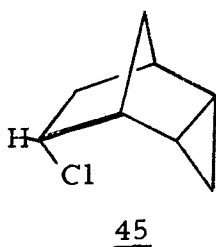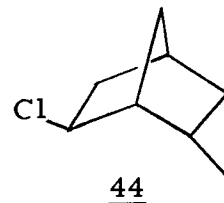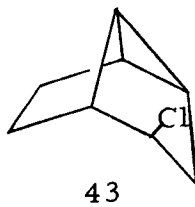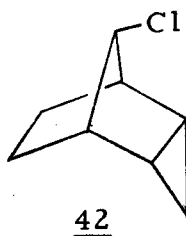
Also there was no similarity to the spectrum of the syn-alcohol and

the syn-methyl ether. The spectrum also showed no resemblance

to that of the rearranged exo-alcohol. The α-hydroxy proton in the

latter alcohol appears as a doublet (71). We can therefore rule out

the rearranged exo-chloride structure 43. The absence of any

signal for cyclopropane methylene protons would rule out the exo-

6-chloride 44 and the endo-6-chloride 45. We could also rule out

substitution at the cyclopropyl C_3 position since the α-chloro proton

in such a case would be expected to absorb in the neighborhood of

τ7.0 (80, 81), even after correcting for the fact that the cyclo-

propane methylene protons in the endo-system have a lower chemical

shift than their counterpart in the exo-system.

Since we observed the formation of several chlorides in this reaction, contrary to Fenwick's report, it became imperative to ascertain whether the three chlorides (the rearranged endo-chloride and the two unidentified chlorides) were the resultants of secondary reactions, viz., the products of isomerization of the anti-chloride. In order to clear up this point, a pure sample of the anti-chloride was subjected to the reaction conditions, i.e., irradiated in carbon tetrachloride solution with added acetone and t-butanol for 20 minutes. Analysis by vpc and 100 MHz nmr revealed that the anti-chloride had not suffered any detectable change. We could have easily detected about 1% of isomerization or rearrangement. The rearranged endo-chloride was also similarly found to be stable to the reaction conditions. Both the chlorides were also found to be homogeneous on several vpc columns of divergent polarity (col 1-5). The 5% component was also found to be stable to the vpc conditions. This demonstrable stability of the chlorides clearly vouchsafed for the fact that all the observed chlorides were primary products of the photochlorination reaction.

At this point, the stereospecificity of the products looked impressive enough to attract a consideration of the following two possible mechanistic situations.

1. An equilibrating pair of classical radicals.
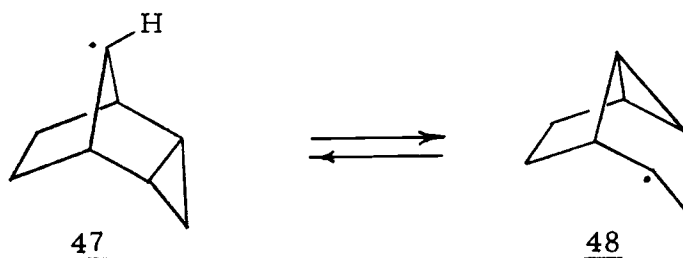
2. A single non-classical radical intermediate.
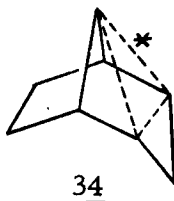
Either of these could nicely explain the products.

The elegant method of Seubold (54) was employed to afford a choice between the above intermediates. This method, which has been availed of by numerous workers to tackle similar problems successfully in the past, consists in varying the concentration of the chain transfer agent and examining the relative proportions of the rearranged and unrearranged products. If the intermediate involved is a single delocalized intermediate, then changes in the concentration of the chain transfer agent should not affect the relative proportions of the rearranged and unrearranged products. On the contrary, if a pair of classical radicals is implicated, then progressive dilution of the chain transfer agent would, by allowing more time for the

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initially formed radical to rearrange, lead to increasing proportions of the rearranged product relative to the unrearranged one. A better appreciation of this method can be gained by examining the kinetic expressions for the respective intermediates, derived below.

A. <u>An equilibrating pair of classical radicals.</u>

t-BuO· +   I   ⟶   II

II ⇌ III k_1 / k_{-1}

II + t-BuOCl →k_2 V + t-BuO·

III + t-BuOCl →k_3 VI + t-BuO·

B. A single non-classical radical intermediate.

$$I + t\text{-}BuO\cdot \longrightarrow IV$$

$$IV + t\text{-}BuOCl \xrightarrow{k_4} V + t\text{-}BuO\cdot$$

$$IV + t\text{-}BuOCl \xrightarrow{k_5} VI + t\text{-}BuO\cdot$$
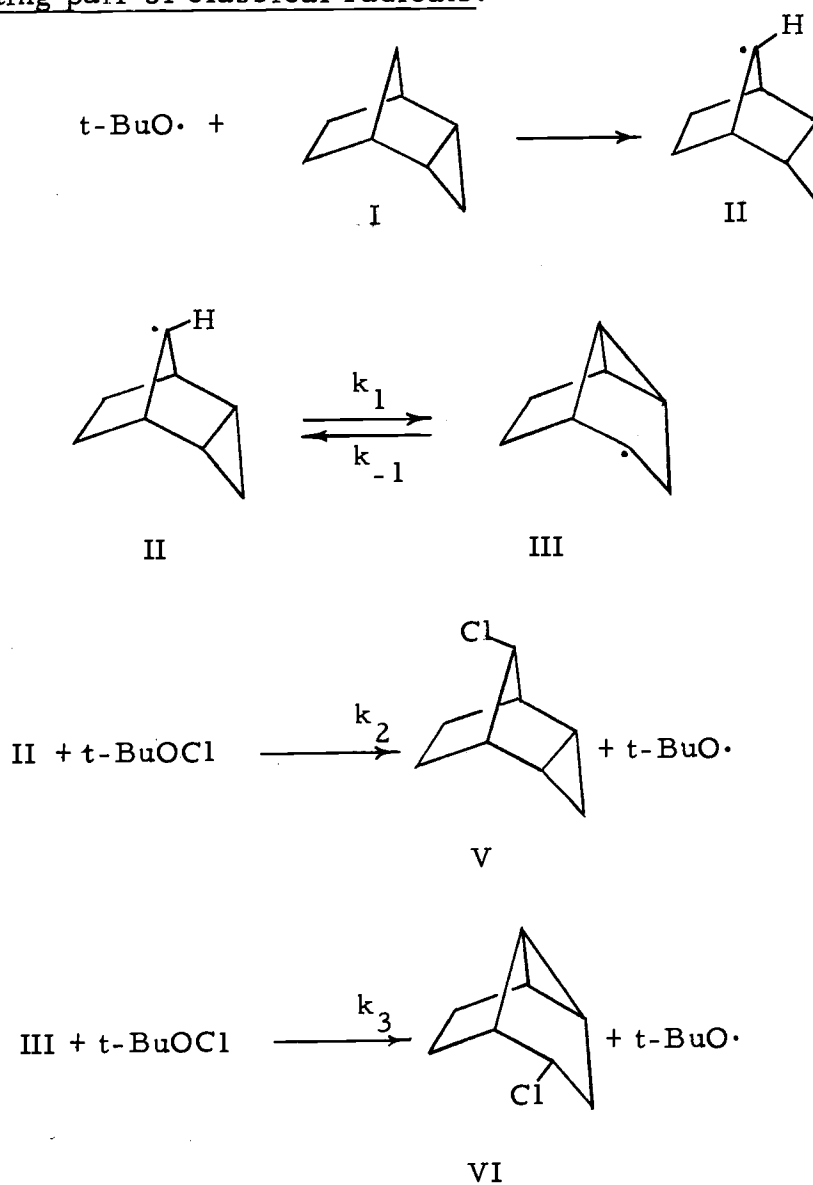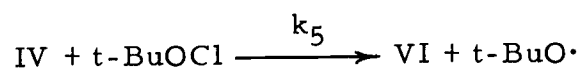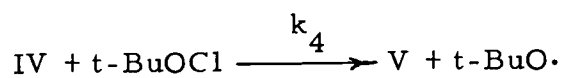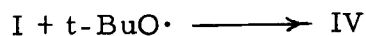
For Case B,
$$\frac{d(V)}{dt} = k_4 (IV)(t\text{-}BuOCl)$$

$$\frac{d(VI)}{dt} = k_5 (IV)(t\text{-}BuOCl)$$

$$\frac{d(VI)}{d(V)} = \frac{k_5(IV)(t\text{-}BuOCl)}{k_4(IV)(t\text{-}BuOCl)}$$

$$\frac{(VI)}{(V)} = \frac{k_5}{k_4}$$

$$= \text{constant}$$

Hence the relative proportions of the rearranged and unrearranged products should be independent of the concentration of t-butylhypochlorite, if a single delocalized intermediate is involved.

For Case A,
$$\frac{d(V)}{dt} = k_2(II)(t\text{-}BuOCl)$$

$$\frac{d(VI)}{dt} = k_3(III)(t\text{-}BuOCl)$$

Considering the equilibrium between II and III,
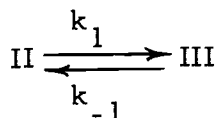
$$II \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} III$$

and reminding ourselves of the process

$$\text{III} + \text{t-BuOCl} \xrightarrow{\text{k}_3} \text{VI} + \text{t-BuO} \cdot$$
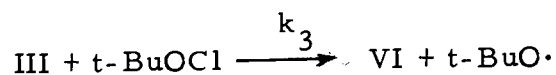
Rate of formation of III $= k_1(\text{II})$

Rate of consumption of III $= k_{-1}(\text{III}) + k_3(\text{III})(\text{t-BuOCl})$

Applying the steady state principle, these two rates may be set equal.

$$k_{-1}(\text{III}) + k_3(\text{III})(\text{t-BuOCl}) = k_1(\text{II})$$

$$(\text{III})\left[k_3(\text{t-BuOCl}) + k_{-1}\right] = k_1(\text{II})$$

$$(\text{III}) = \frac{k_1(\text{II})}{k_3(\text{t-BuOCl}) + k_{-1}}$$

Substituting the R·H·S· for (III) in the expression for $\dfrac{d(\text{VI})}{dt}$, we get

$$\frac{d(\text{VI})}{dt} = \frac{k_1(\text{II})k_3(\text{t-BuOCl})}{k_3(\text{t-BuOCl}) + k_{-1}}$$

If k_{-1} is very large compared to $k_3(\text{t-BuOCl})$, the above expression reduces to

$$\frac{d(\text{VI})}{dt} = \frac{k_1(\text{II})k_3(\text{t-BuOCl})}{k_{-1}}$$

$$\frac{(\text{VI})}{(\text{V})} = \frac{k_1(\text{II})k_3(\text{t-BuOCl})}{k_{-1}k_2(\text{II})(\text{t-BuOCl})}$$

$$= \frac{k_1 k_3}{k_{-1} k_2}$$

$$= \text{constant.}$$

i.e. , the results of a rapid equilibrium between II and III could not

be distinguished from the single mesomeric intermediate situation.

If $k_3(t\text{-BuOCl})$ is $\gg k_{-1}$, then

$$\frac{d(VI)}{dt} = \frac{k_1(II)k_3(t\text{-BuOCl})}{k_3(t\text{-BuOCl})}$$

$$= k_1(II)$$

Hence,
$$\frac{(VI)}{(V)} = \frac{k_1(II)}{k_2(II)(t\text{-BuOCl})}$$

$$= \frac{k_1}{k_2(t\text{-BuOCl})}$$

Therefore the ratio of the rearranged to the unrearranged chloride

should be inversely proportional to the concentration of t-butylhypo-

chlorite. If k_{-1} and $k_3(t\text{-BuOCl})$ are of comparable magnitude, then

the ratio of the rearranged to unrearranged chloride will change, but

not necessarily in accordance with the above equation.

In pursuance of this approach, several photochlorination runs

were made, allowing the endo-hydrocarbon to react with widely

varying concentrations of t-butylhypochlorite and the relative pro-

portions of the monochlorides were estimated by a combination of

vpc and nmr analysis. The results of these experiments are shown

in Table 2.

Table 2. Effect of varying the concentration of t-butylhypochlorite on the relative proportions
of the chlorides

Run	Molality of endo-hydrocarbon	Molality of t-BuOCl	Anti-chloride 17[a]	Rearranged endo-chloride 16[a]	Unidentified chloride A[a,c]	Unidentified chloride B[a,b]
1	1.56	0.68	66	27	5	2
2	1.56	0.49	63	28	6	3
3	1.56	0.26	32	41	11	16
4	0.73	0.18	11	56	15	18

[a] $\pm 3\%$.

[b] Unisolable component.

[c] Component which was incompletely characterized.

The results of the dilution experiments throw much light on
the nature of the radical generated. By using a higher concentration
of t-butylhypochlorite, we are able to trap more and more of the
initially formed radical. Clearly the non-classical radical as a
single intermediate can be ruled out. Interestingly the proportions
of the incompletely characterized component A and the unisolable
component B increase on dilution of t-butylhypochlorite. Apparently
these two chlorides also arise from abstraction at the δ-position.
It is possible that B is the syn-chloride 42.

Now the question arises: Can the representation of the reac-
tion course as proceeding through a rapidly equilibrating pair of
classical radicals adequately explain the observations?

47   48
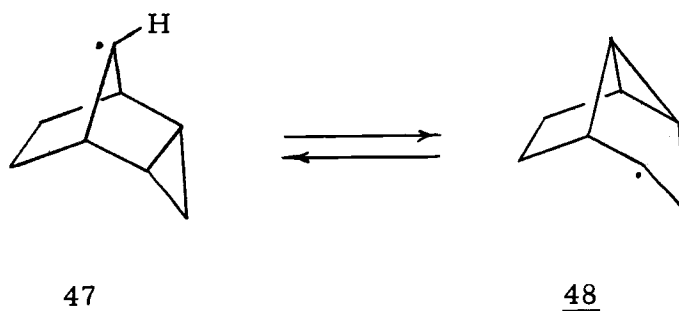
A pair of classical species equilibrating rapidly might engender a
"wind-shield wiper" effect, thereby preventing or minimizing capture
from the syn-face in 47 and from the exo-face in 48. This type of
explanation was originally advanced by Brown (see Chapter I) for
explaining the stereospecific formation of products from carbonium

ions as an alternative to the non-classical mesomeric species. But

this hypothesis did not find favor with the chemists who doubted

whether such an explanation could convincingly account for the nearly

100% stereospecificity of the carbonium ion products (91). In the

present case, it is easily seen that the reaction of the unrearranged

radical is, although perhaps not completely ($\geqslant 66/2$), predominantly

from the anti-side. The rearranged radical however undergoes

chain transfer almost completely from the endo-direction ($\geqslant 27/2$).

Inspection of molecular models shows that the sterically more favor-

able direction for reaction is the exo-side. This is amply borne out

by the observation that lithium aluminum hydride reduction of the

rearranged ketone 49 yields exclusively the rearranged endo-alcohol

15, demonstrating that hydride attack occurs exclusively from the
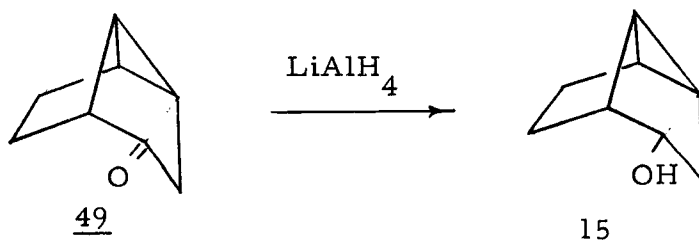
exo-direction (17). In the light of these facts, we have to infer that

the chain transfer of the rearranged radical is not governed by simple

steric considerations. It is possible to explain the experimental

observation by suggesting a rapidly equilibrating pair of classical

radicals. Although we have eliminated the non-classical radical as a

single product-determining intermediate, it may be that we cannot

rule out a role for it as one of the intermediates. The stereospecific

reaction of the rearranged radical may represent one of the rare

instances where transannular participation of a β-cyclopropane ring

is chemically significant. The initially formed intermediate with a

radical center at the 8-position (50) could well be a pyramidal radical

whose inversion would be expected to be slow on account of the unfav-

orable bond angle at this position. This radical could then go over

to or be in equilibrium with the delocalized radical 34.
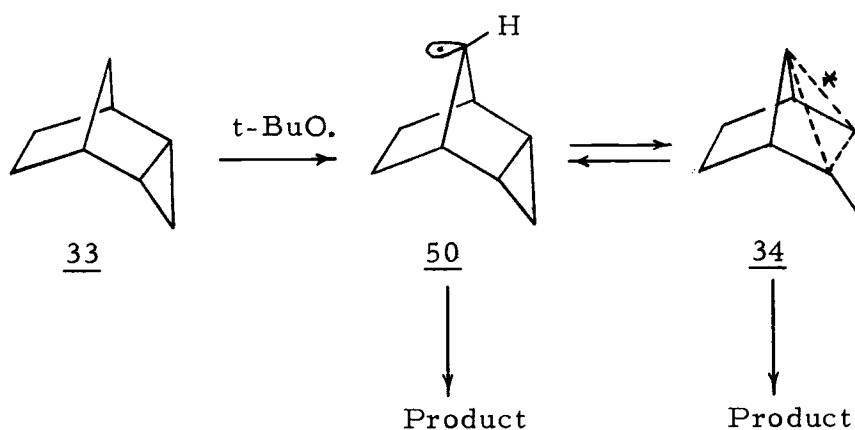
In the fitness of things, it was but desirable to generate the

rearranged radical by other independent routes and follow the course

of its destiny. It appeared that this objective could be most conveni-

ently accomplished by dispossessing the rearranged endo-chloride

of its chloro substituent by employing tri-n-butyltin hydride (TBTH).

Accordingly this chloride was reduced with TBTH with AIBN initiation

at 95±2° . Analysis by vpc, ir and nmr showed the presence of only

one hydrocarbon product in a yield of 65% (versus cyclohexane

standard). The sole product was identified as tricyclo$[3.3.0.0^{4,6}]$-

octane 51 by comparison of vpc retention time, ir, and nmr spectra

with those of an authentic sample. We could not detect any of the

endo-hydrocarbon 33. This result only bears further testimony to

the conclusion drawn earlier that a single non-classical intermediate

can be ruled out.
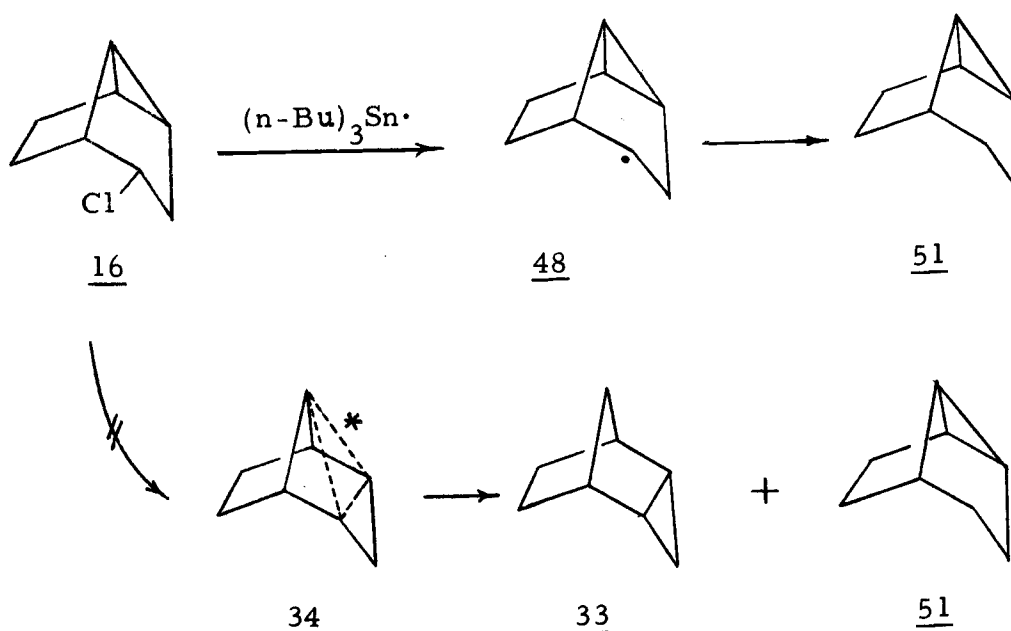
Another facile route to the rearranged radical was the radical

reduction of the rearranged dichloride 52 (whose synthesis is

described later in this chapter) with TBTH. It is common knowl-

edge that cyclopropyl radicals are formed very sluggishly, relative

to other radicals. It would hence be expected that in the dichloride

52 the chlorine that would be susceptible to facile removal under

radical conditions would be the one at the secondary position and

this would result in the generation of the desired radical intermediate.
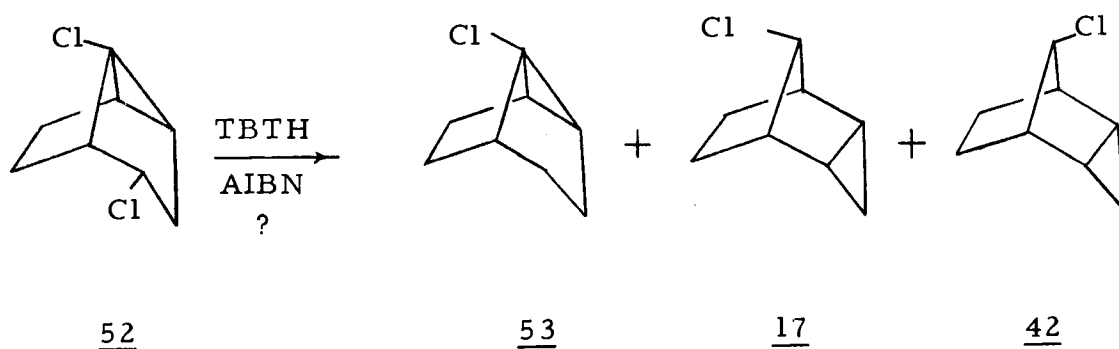
An attractive, but seemingly remote, possibility was that a reverse

rearrangement of this radical might yield the syn- and anti-chlorides

(42 and 17) which had thus far eluded all attempts at synthesis. With

a view to testing these possibilities, the dichloride was submitted to

an AIBN-initiated reduction with TBTH at $95\pm2°$. Vpc analysis of

the products showed that the products were composed of three com-

ponents in the ratio 10:83:7 in the order of increasing retention times,

in a total yield of 84% (versus cyclohexane internal standard). The

10% and 7% components were identified as tricyclo[3.3.0.0^{4,6}]octane

51 and the rearranged endo-chloride 16 respectively by comparison

of ir and nmr spectra with those of authentic samples. The 83%

component gave the correct elemental analysis for $C_8H_{11}Cl$ and

the mass spectrum showed parent peaks at m/e 142 and 144. The

ir spectrum lacked bands in the region 1500-1700 cm^{-1}, showing

the absence of C=C double bonds. There were bands at 3040 cm^{-1}

(cyclopropyl C-H stretching) and 765 cm^{-1} (C-Cl stretching). Its

nmr spectrum (100 MHz, CCl$_4$) had resonance signals at τ7.25

(triplet, 1H), 7.65-8.05 (multiplet, 4H), 8.2 (doublet, 2H), and

8.45-8.9 (complex multiplets, 4H). The absence of an α-chloro

proton showed that it was a tertiary chloride. The only conclusion

that could be drawn from these data is that this chloride is 6-chloro-

tricyclo[3.3.0.0^{4,6}]octane 53. The assignment of the signals is as

follows (in the order of increasing τ values): the bridgehead proton

(C_1), the exo-protons on C_2, C_3, C_7, and C_8, the cyclopropyl protons

on C_4 and C_5, and the endo-protons on C_2, C_3, C_7 and C_8.
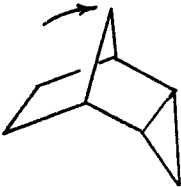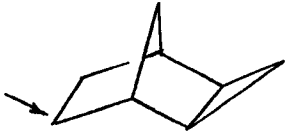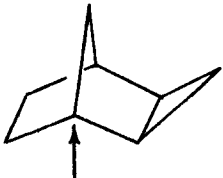
Thus the final results of analysis of the radical reduction of the

dichloride with TBTH are as follows:

| 52 | 53 (83%) | 16 (7%) | 51 (10%) |
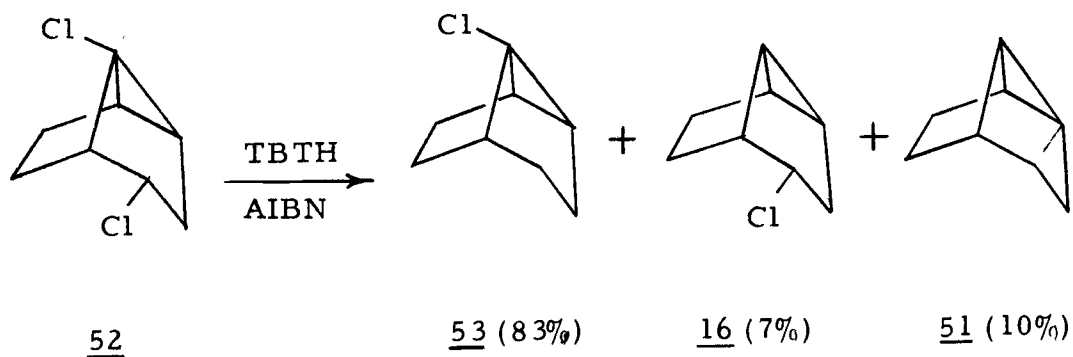
Neither the syn- nor the anti-chloride was detectable. The lack of

reverse rearrangement of the radical intermediate is in keeping

with a similar observation made earlier in the case of the radical

reduction of the rearranged endo-chloride 16. The low proportion

of the rearranged endo-chloride resulting from reduction of the

tertiary chloride and the predominant formation of the tertiary chlor-

ide 53 only bear out the general belief that cyclopropyl radicals are

much more slowly formed than simple alkyl radicals.

With experimental observations in hand militating against the direct formation of a single non-classical radical intermediate, it was still of considerable importance to determine the degree of anchimeric assistance in radical formation in abstraction from endo-tricyclooctane 33 and relate it to hydrogen abstraction rates in exo-tricyclooctane 29. Following the method of Walling and Jacknow (83), we allowed the hydrocarbons to compete with cyclohexane for the t-butoxy radical in order to calculate relative reactivities. The data are summarized in Table 3.

Table 3. Relative rates of hydrogen abstraction vs. cyclohexane at 40±0.5°

Position of Abstraction	Relative Rate[a]	Number of Hydrogens	Relative Rate per Hydrogen[a]
	0.919 ± 0.033[b]	1	11.03 ± 0.40[b]
	0.405 ± 0.036	2	2.43 ± 0.22
	0.087 ± 0.008	2	0.52 ± 0.05

[a]Arithmetic mean and standard deviation of three runs.

[b]Assuming that 93% abstraction occurs at C_8.

It is seen that in both the _exo_- and _endo_-hydrocarbons the major

positions of abstraction correspond to the major positions of carbon-

ium ion stability in these systems. This is in keeping with the trend

observed in the bicyclo[3.1.0]hexane (44) and bicyclo[4.1.0]heptane

(46) systems. Freeman's rationalization of this trend in the bicyclo-

[3.1.0]hexane system would apply in the present case also. Since

the t-butoxy radical is an electonegative species, the transition state

for hydrogen abstraction would be expected to be polarized, conferring

some carbonium ion character on the developing hydrocarbon frag-

ment. Thus, a possible rationalization is that there is trishomo-

cyclopropenyl anchimeric assistance to abstraction of the _anti_-C_8

hydrogen in the _endo_-system and end-on participation in the _exo_-

system. The radical formed after complete removal of the hydrogen

is a classical species.
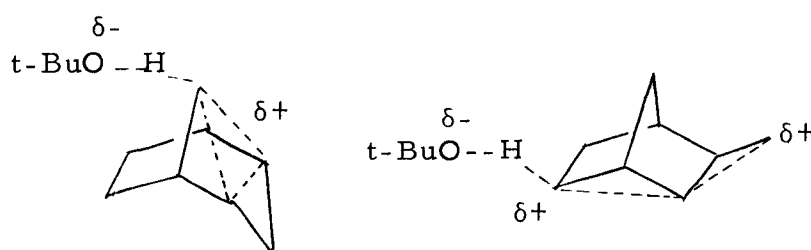
At this point it was felt that in view of the rather high stereo-

specificity of the chloride products from the radical center generated

at C_8 in the _endo_-system, an unambiguous independent synthesis of

the _endo_-_syn_-8- and _endo_-_anti_- 8-chlorides would help to clarify the

situation further. The first method tried was the reaction of a

mixture of the syn- and anti-alcohols 14 (64% syn-, 36% anti-) with

thionyl chloride in ether. Work-up followed by vpc analysis showed

that there was only one product in a yield of 80%. The vpc retention

time and ir spectrum of this sole product were identical to those of

an authentic sample of the rearranged endo-chloride 16. Neither

the syn- nor the anti-chloride was detectable. A few comments on

the mechanism of the reaction would now be appropriate. The

14
(64% syn, 36% anti)

16
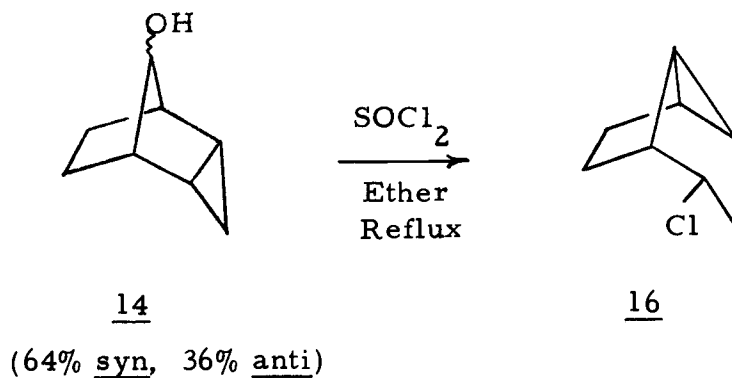
reaction of alcohols with thionyl chloride in inert solvents, commonly

referred to as an $S_N i$ reaction (substitution, nucleophilic, internal) was,

for a long time, thought to be a one-step process. However, after
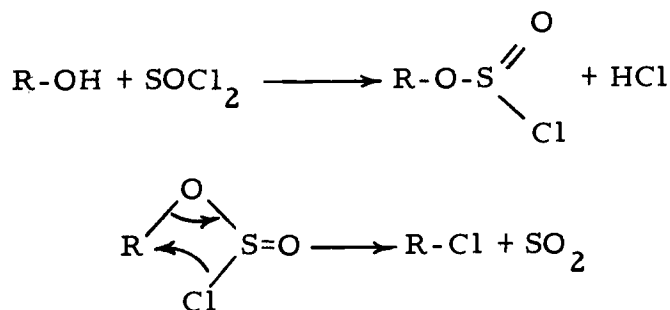
reports by several workers (92, 93), of the obtention of rearranged

product in this reaction, chemists have been entertaining the notion

that an ion pair intercedes in the reaction. It is not surprising then
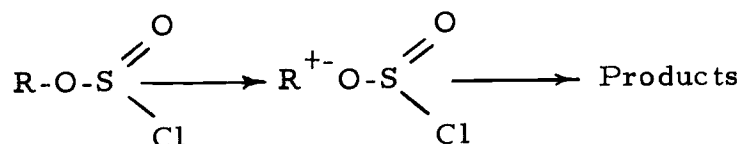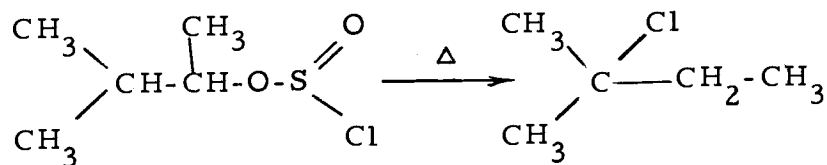
that we observed the formation of the rearranged chloride exclusively.
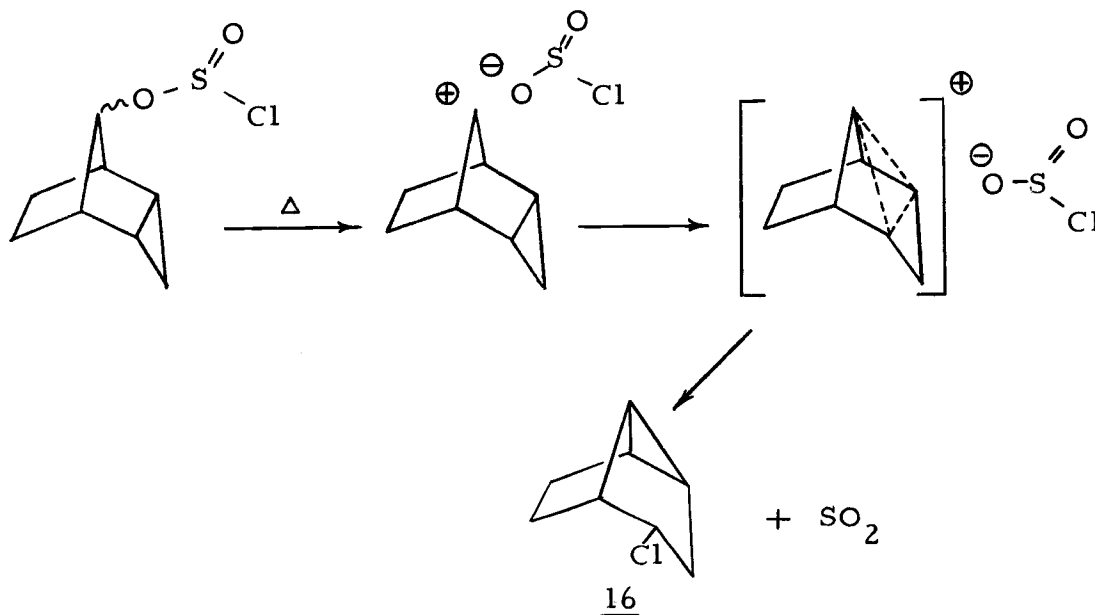
It is a matter of general observation that the addition of

pyridine to a mixture of alcohol and thionyl chloride culminates

in the formation of alkyl halide with inverted configuration. Inver-

sion is a consequence of the reaction of pyridine with ROSOCl to

give $ROSO\overset{+}{N}C_5H_5$ before anything further can occur. The Cl^- ion

formed in this process now attacks from the backside. Such a pro-

cedure, if carried out on a mixture of the syn- and anti-alcohols 14,

could possibly yield a mixture of the anti- and syn-chlorides. This

possibility was tested by heating the mixture with alcohols in the

presence of a slight molar excess of pyridine, with thionyl chloride

at 60°. Work-up followed by vpc analysis showed that there was

only one product, formed in a yield of 64%. The ir and nmr spectra

were identical to those of an authentic sample of the rearranged

endo-chloride 16. Apparently, the $S_N i$ process had occurred to the
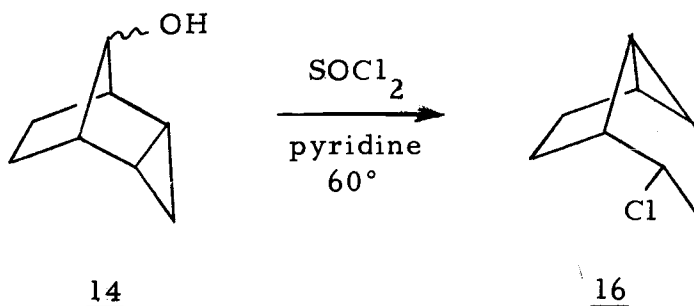
exclusion of the $S_N 2$ process, thus frustrating our effort.

A third approach was suggested by the recent reports of Weiss

and Snyder (86-88) on the conversion of alcohols to chlorides using

triphenylphosphine and carbon tetrachloride. The mixture of alcohols

14 was separated by preparative vpc and each of the individual alco-

hols was stirred with triphenylphosphine and carbon tetrachloride

at room temperature followed by removal of solvent at reduced

pressure and pyrolysis of the phosphorane ester at 140-150°.

The products from the syn-alcohol were found by vpc analysis

to be composed of two major components in the ratio 32:48 in the

order of increasing retention times in a yield of 41%. About five

small fractions accounted for the remaining 20% of the products.

The 32% component had vpc retention time, ir, and nmr spectra

identical to those of an authentic sample of the rearranged endo-

chloride 16. The 48% component seemed to be undergoing slow

decomposition on prolonged exposure to air. Its elemental analysis

corresponded to the formula $C_8H_{12}O$. Its ir spectrum showed the

presence of a C=C double bond (a weak band at 1640 cm^{-1}, a medium-

sized band at 3029 cm^{-1}) and of an aldehyde group (a medium-sized

band at 2719 cm^{-1}, characteristic of aldehydic C-H stretching), and

a strong band at 1716 cm^{-1} (attributable to carbonyl group). The

nmr spectrum (100 MHz, CCl_4) contained resonance signals at

τ0.45 (singlet, 1H), 4.3 (unresolved triplet, 2.0 H) and τ7.4-8.8

(complex multiplets, 9 H). The signal at τ0.45 confirmed that the

compound was an aldehyde. The spectrum appeared to belong to a

compound of symmetrical structure. The absence of cyclopropane

ring suggested that this compound should have arisen from a deep-

seated rearrangement of the starting tricyclic system. A structure

that would nicely fit the spectral data is Δ^4-cycloheptenylcarboxalde-

hyde 54. Convincing proof of this assignment was secured by
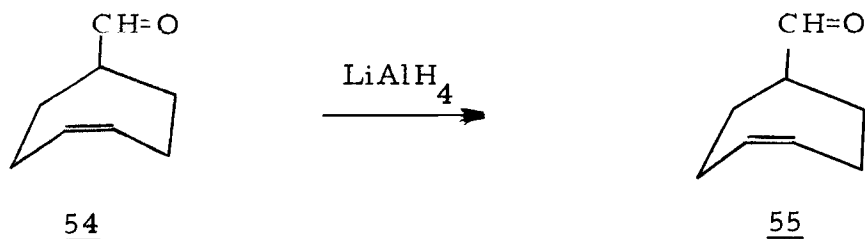
reduction of this aldehyde with lithium aluminum hydride which

yielded Δ^4-cycloheptenylmethyl alcohol 55, identified by comparison

of vpc retention time, ir, and nmr spectra with those of an authentic

sample (94). The anti-alcohol on subjection to similar treatment gave

45% of the aldehyde 54 and 55% of the rearranged endo-chloride 16

in a yield of 39%.
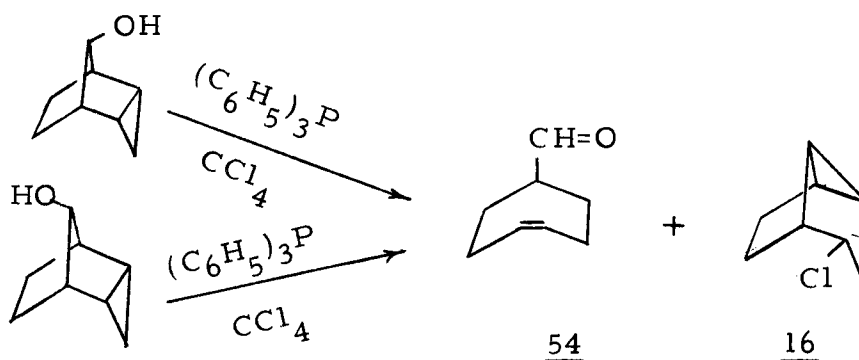
The possibility that the rearranged chloride 16 could be the result

of rearrangement of the anti-chloride 17 was dismissed by the obser-

vation that 17 did not suffer any detectable change on submission to

the reaction conditions.

A few comments on the mechanism of this reaction would not

be out of place here. Observing that the decomposition of the phos-

phorane ester shows first order kinetics and that external nucleo-

philes do not compete with chloride, Weiss and Snyder (87, 88)
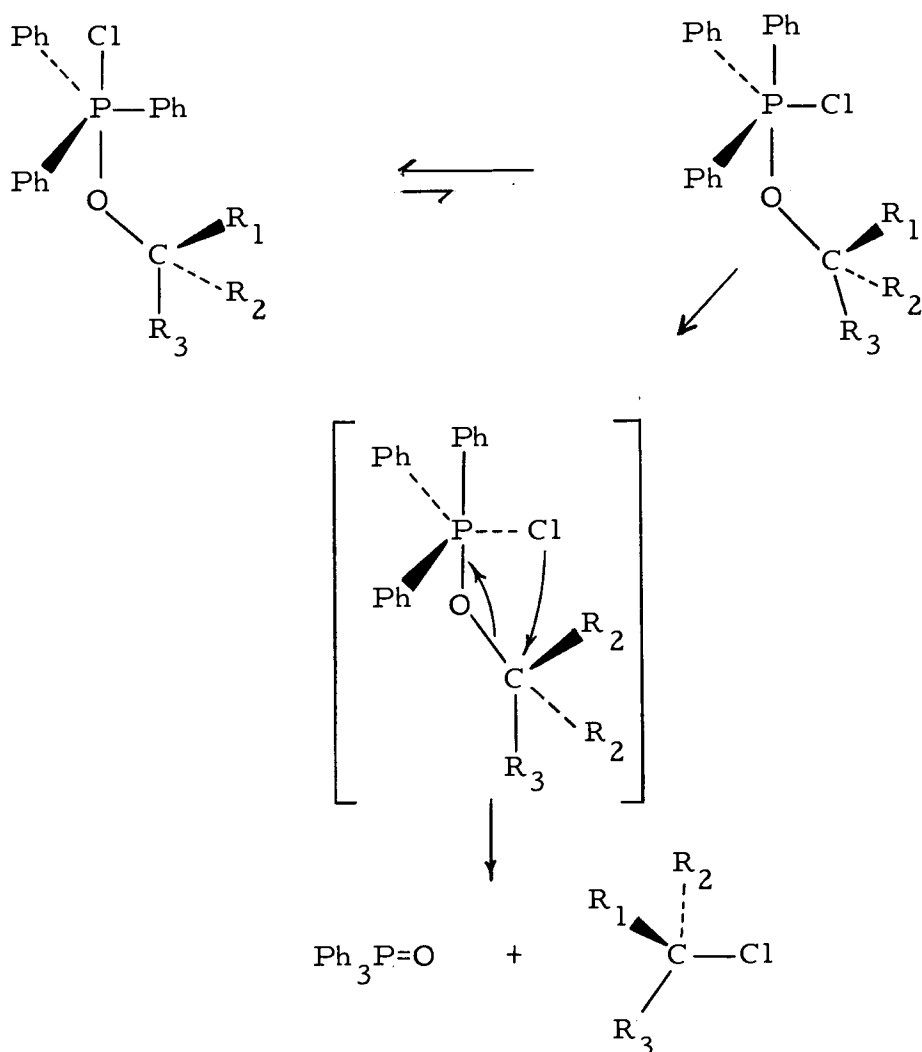
suggest that the product (inverted chloride) could be formed by a reasonably concerted, intramolecular decomposition of the phosphorane ester having the pentacovalent phosphorus as a trigonal bipyramid with the chlorine or oxygen in the equatorial conformation and that P-Cl bond cleavage could precede somewhat C-O bond cleavage in a very tight ion pair. The authors also noted that this inversion pathway occurs either predominantly or significantly, competing with the carbonium ion process. The former requires

precedence of C-Cl bond breakage over C-O cleavage while the latter requires a reversal of this order. The exclusive formation of the rearranged chloride in our case clearly implicates a carbonium ion (or ion pair) pathway as the sole route to the chloro product. This is very similar to the case of the reaction of the syn- and anti-alcohols with thionyl chloride in ether which yielded the rearranged chloride exclusively. Clearly when a very stable carbonium ion can be formed, the inversion pathway may be completely excluded. Contradicting Snyder's claim, this is the first recorded instance of the total exclusion of the inversion pathway in this reaction.

Adverting to the formation of Δ^4-cycloheptenyl carboxaldehyde from both the syn- and anti-alcohols, it may be observed that there is no precedent for the formation of an aldehyde in the reaction of alcohols with triphenylphosphine and carbon tetrachloride. The formation of the aldehyde from both the syn- and anti-alcohols requires that the decomposition of the oxyphosphorane ester also simultaneously traverses another mechanistic route. The experimental observation could possibly be accommodated by the following mechanism.
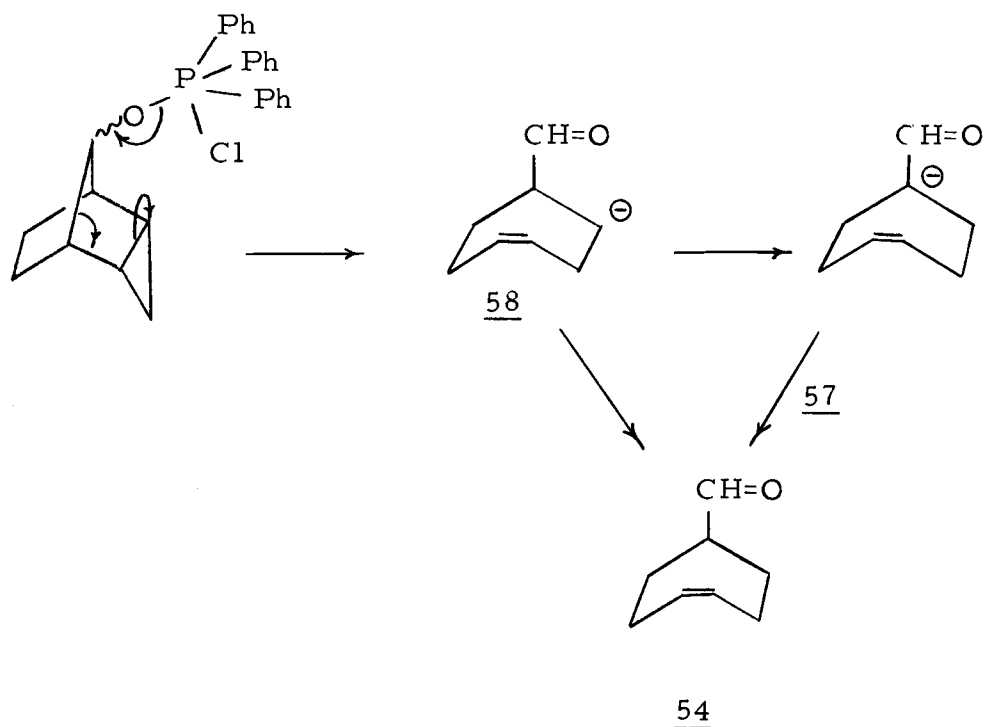
This mechanism invoking P-O bond cleavage is however entirely speculative and bristles with difficulties. It is not clear, for example, why aldehyde formation arising from this type of cleavage has not been observed in the other systems studied so far. Another ticklish question pertains to the origin of the proton needed for the neutralization of the carbanion 56 or 57.

Another possible mechanism for the formation of the aldehyde involves formation of the alkoxide 58 from the phosphorane ester followed by a concerted, symmetry-allowed 1, 3-sigmatropic shift of C_8, with inversion at C_8, to give the alkoxide anion 59. The alkoxide anion 59 could then rearrange by cyclopropane ring opening

to the aldehydes 54 or 60.
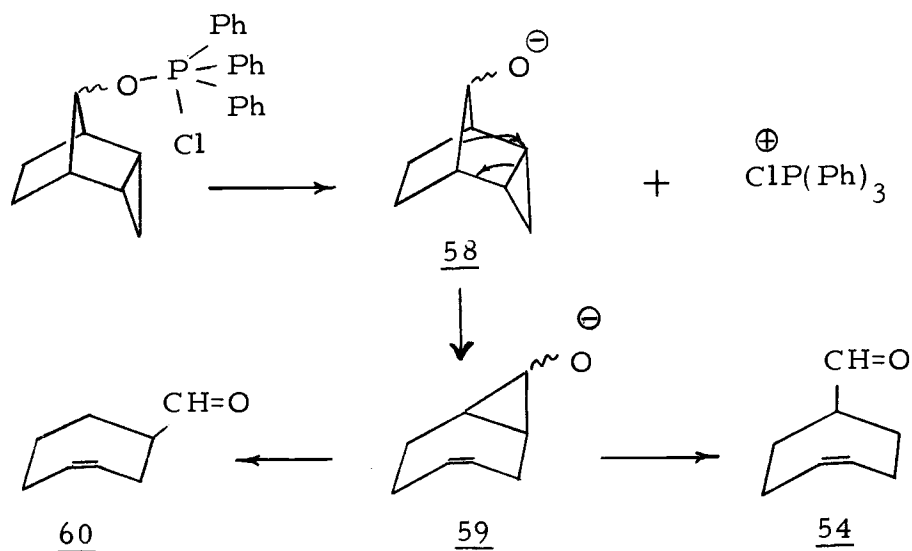
This mechanism is similar to the first stage of the mechanism sug-
gested by Franzus and his coworkers (95) for the formation of methyl
tropyl ether in the reaction of 7-acetoxynorbornadiene with methoxide
or hydroxide ions.
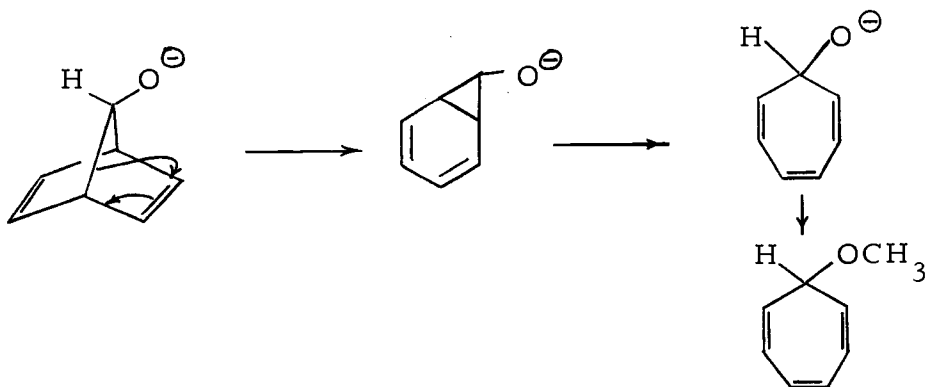
However, the obtention of only one aldehyde product in the present
case would seem to argue against this mechanism which predicts the
formation of two aldehydes. The possibility that the aldehyde 60 is

unstable to the reaction conditions or vpc could not be tested due to

its non-availability and consequently the failure to observe this

product would not suffice to rule out this mechanism. Clearly

further work will be needed in order to elucidate the mechanism

of this interesting process.

The exclusive formation of the rearranged product that besets

any process proceeding through a carbonium ion (or ion pair) at the

8-position in this system led us to devise a process involving a free

radical intermediate. It was felt that removal of a chlorine atom

by radical reduction of 8, 8-dichloro-endo-tricyclo[3. 2. 1. 0^{2,4}]octane

61 with tri-n-butyltin hydride (TBTH) might yield the desired result,

if the reduction is halted at the monoreduction stage.
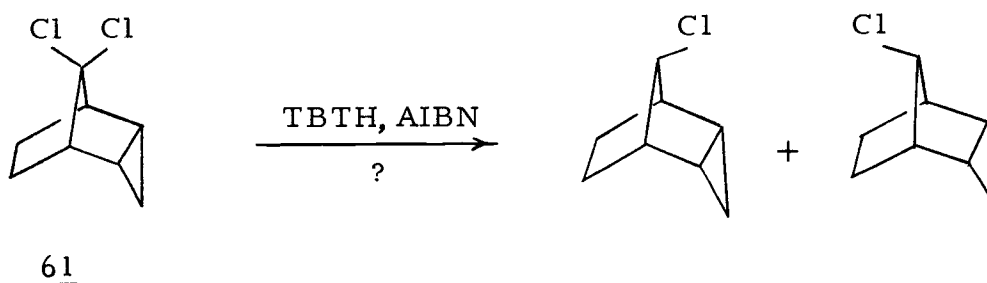
A well-known route to gem-dichlorides involves the reaction

of ketones with phosphorus pentachloride (96). In pursuance of this

approach, the endo-ketone 5 was allowed to react with phosphorus

pentachloride in carbon tetrachloride solution at reflux temperature.

$$R-\overset{\overset{\textstyle O}{\|}}{C}\ R' \quad\xrightarrow{\ PCl_5\ }\quad R-\overset{\overset{\textstyle Cl\ \ Cl}{\diagdown\diagup}}{C}-R'$$
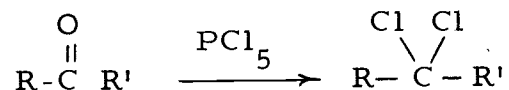
Work-up followed by vpc analysis revealed the presence of only one

product, formed in a yield of 60.5%. The ir spectrum of this product

was devoid of bands in the region 1500-1700 cm^{-1} showing the absence

of C=C double bond. A weak band at 3048 cm^{-1} indicated the presence

of cyclopropane ring. Intense bands at 812 and 75 cm^{-1} revealed the

presence of C-Cl linkage. The nmr spectrum (100 MHz, CCl_4)

showed a six-peak one proton signal at τ5.48-5.73, identical in its

splitting pattern to that of the α-chloro proton in the rearranged

endo-chloride 16. Complex multiplets between τ7.05 and 8.7 inte-

grating to nine protons accounted for the remainder of the spectrum.

The presence of the α-chloro proton and the absence of cyclopropane

methylene protons leave no doubt that the dichloride in question is

the rearranged dichloride 52 and not the gem-dichloride 61.

$$5 \qquad\qquad \xrightarrow{\ PCl_5,\ CCl_4\ }\qquad\qquad 52$$
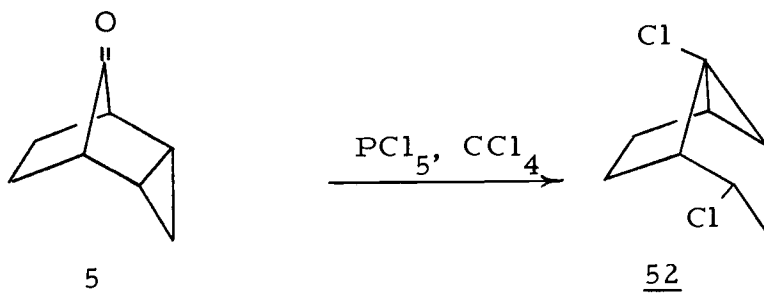
The mechanism of the reaction of ketones with phosphorus

pentachloride is the subject of a recent report by Newman (97).

According to Newman, the ketone reacts with phosphorus

pentachloride to form a complex which could then collapse by a

concerted intramolecular process or by a carbonium ion (or ion pair)

process to give unrearranged and/or rearranged dichloride (Scheme

4). In view of the proclivity of our system to form the carbonium ion

(or ion pair), it is small wonder then that we observed the formation

of the rearranged dichloride exclusively.

<u>Scheme 4</u>
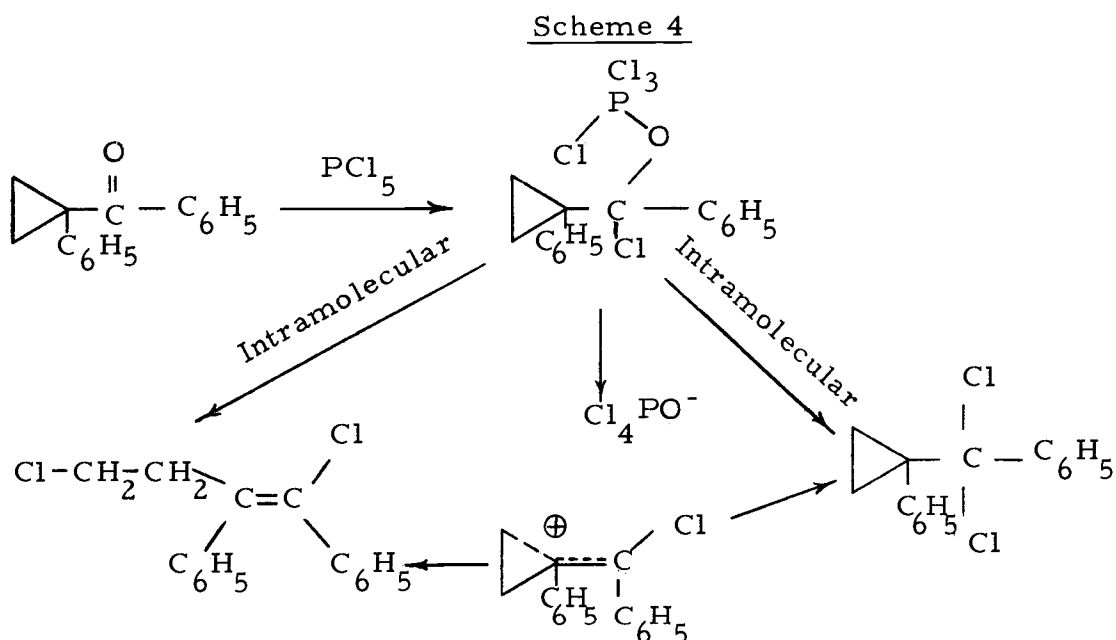
The disturbing crop of failures resulting from the synthetic

efforts prompted the feeling that any further attempt in this direction

might turn out to be futile and that a return to the free radical study

would be more profitable. At this point it was felt that it would help

to characterize the radical intermediates more thoroughly if they

could be generated by other independent routes. It was reported by

Toebler and his co-workers (57) that the reaction of norbornene with

t-butylhypochlorite results in both addition and substitution, addition

predominating. Encouraged by this report, we felt that the reaction

of the endo-olefin 62 with t-butylhypochlorite might enable us   to

accomplish this objective.
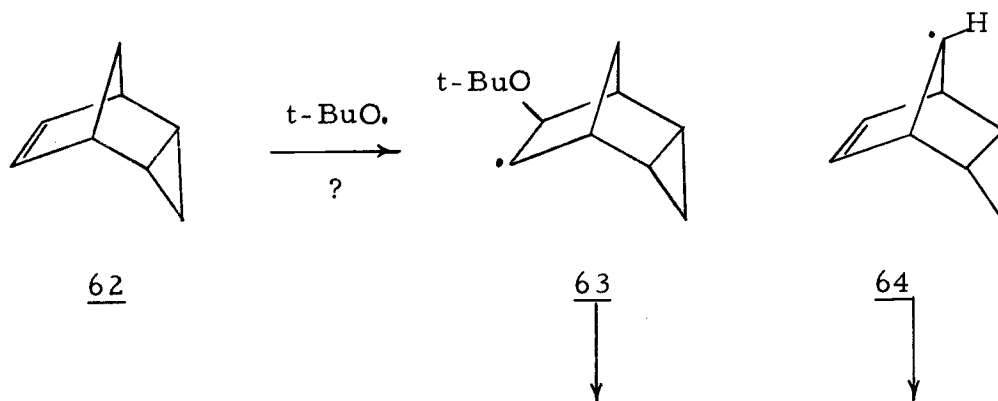
Radical addition to the double bond might generate a radical center

at the 6-position--a feature that was missed in the abstraction study.

Hydrogen abstraction might concurrently occur--at C_8 by analogy to

the saturated hydrocarbon.

When the endo-olefin was irradiated with t-butylhypochlorite

using a 2:1 molar ratio of olefin to the hypochlorite in carbon tetra-

chloride solution at 40°, the products on vpc analysis were found

to consist of two components in the ratio 43:57 in the order of

increasing retention times, in a yield of 59%. The retention times

of the two components were much longer than would be expected of

monochlorides, suggesting that these were possibly the free radical

adducts. The monochloro region in the chromatogram was

conspicuously free of peaks, indicating absence of hydrogen abstrac-

tion.

The ir spectrum of the 43% component (Figure 15) showed weak

bands at 3096 and 3040 cm^{-1} (cyclopropyl C-H stretching), intense

bands at 1190, 1125, 1096, 1065, and 1045 cm^{-1} (C-O stretching) and

somewhat weak bands at 783, 770, 748, and 736 cm^{-1} (C-Cl stretch-

ing). The nmr spectrum (Figure 16, 100 MHz, CCl_4) exhibited

resonance signals at τ6.24 (doublet of a triplet, J-3.4 Hz, 0.7 Hz,

1H), 6.58 (broad singlet, $W_{\frac{1}{2}} = 5$ Hz, 1H), 7.5 (envelope, 1 H), 7.9

(envelope, 1 H), 8.0 (a broad singlet, 2H), 8.28 (a pair of overlapping

triplets of a doublet, J = 7 Hz, 3 Hz, 1H), 8.55-8.75 (multiplet, 2H),

8.82 (singlet, 9H), and 9.15 (multiplet, 1H). The spectrum is con-

sistent with the structure of the trans-adduct, exo-6-t-butoxy-endo-

7-chloro-endo-tricyclo[3.2.1.0^{2,4}]octane, 65 with the assignment

of the signals as shown.

65
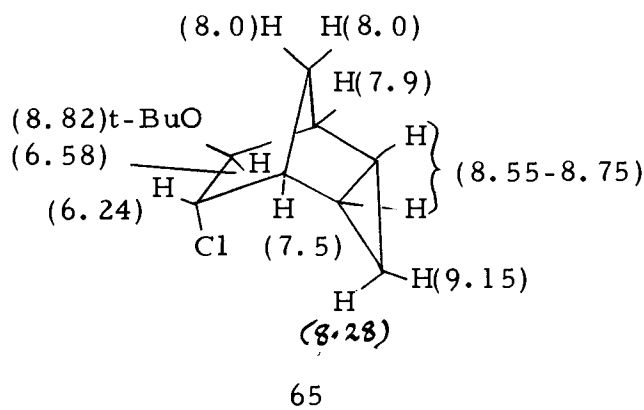
(absence of C=C double bands), intense bands at 1190, 1114, 1104, 1075, 1042, and 1000 cm^{-1} (C-O stretching, the last two also assignable to cyclopropane ring deformation), intense bands at 780, 770, 757, 750 and 718 cm^{-1} (C-Cl stretching). The nmr spectrum (Figure 18, 100 MHz, CCl$_4$) had signals at τ6.36 (doublet of a doublet, J=5.6 Hz, 1.7 Hz, 1H), 6.68 (doublet of a doublet, J=5.6 Hz, 1.7 Hz, 1H), 7.68 (envelope, 1H), 7.73 (A component of an AB pattern, J=9.5 Hz, 1H), 7.92 (envelope, 1H), 8.15 (multiplet of the B doublet of the AB pattern, J=9.5 Hz, 1H), 8.60-8.80 (multiplet, 2H), 8.82 (singlet, 9H) and 9-9.35 (complex multiplet, 2H). The spectrum is consistent with the structure of the cis-adduct, exo-6-t-butoxy-exo-7-chloro-endo-tricyclo[3.2.1.0^{2,4}]octane, 66, with the assignment of the signals as shown.

66
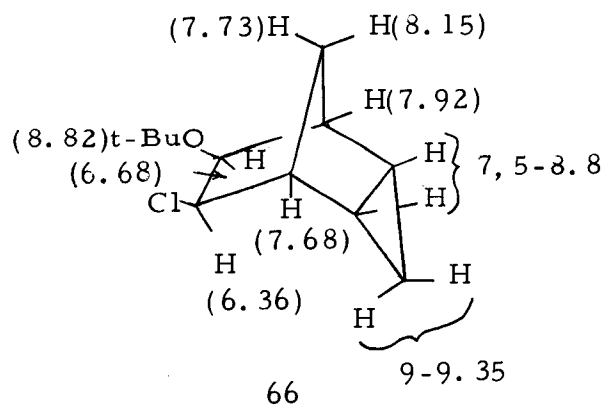
A very convenient verification of these structure assignments was possible by the TBTH reduction of the two adducts. Radical

reduction of both the adducts followed by vpc analysis showed that

the same exclusive product, viz., exo-6-t-butoxy-endo-tricyclo-

[3.2.1.0^{2,4}]octane 67 resulted from both in yields of 75% from the

trans-adduct and 97% from the cis-adduct.
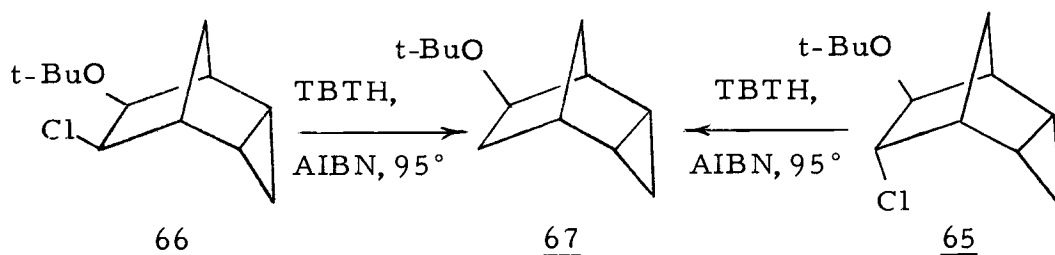
The ir spectrum (Figure 19) of the product from both the adducts

showed absorptions at 3064 cm^{-1} (weak) and 3016 (shoulder), both

assignable to cyclopropyl C-H stretching, and 1194 (s), 1086 (s), and

1030 (s), all three assignable to C-O stretching. The nmr spectrum

(Figure 20, 100 MHz, CCl$_4$) showed signals at r6.74 (doublet of a

doublet, J=6.4 Hz, 3.0 Hz, 1H, the α-t-butoxy proton), 7.8 (unre-

solved multiplet, 1 H, the bridgehead proton β to t-butoxy), 8.0

(unresolved multiplet, 1 H, the other bridgehead proton), 8.2 (broad

singlet, 2H, the C$_8$ protons), 8.6-8.85 (complex multiplets, 4 H,

the protons on C$_7$, C$_2$, and C$_4$), 8.9 (singlet, 9 H, the t-butoxy

protons) and 9.1-9.45 (complex multiplets, 2 H, the C$_3$ protons).

The spectrum showed striking similarity to that of exo-6-hydroxy-

endo-tricyclo[3.2.1.0^{2,4}]octane. Thus the final analysis of the

products of the reaction of the endo-olefin with t-butylhypochlorite

is outlined in Scheme 5 below.

Scheme 5
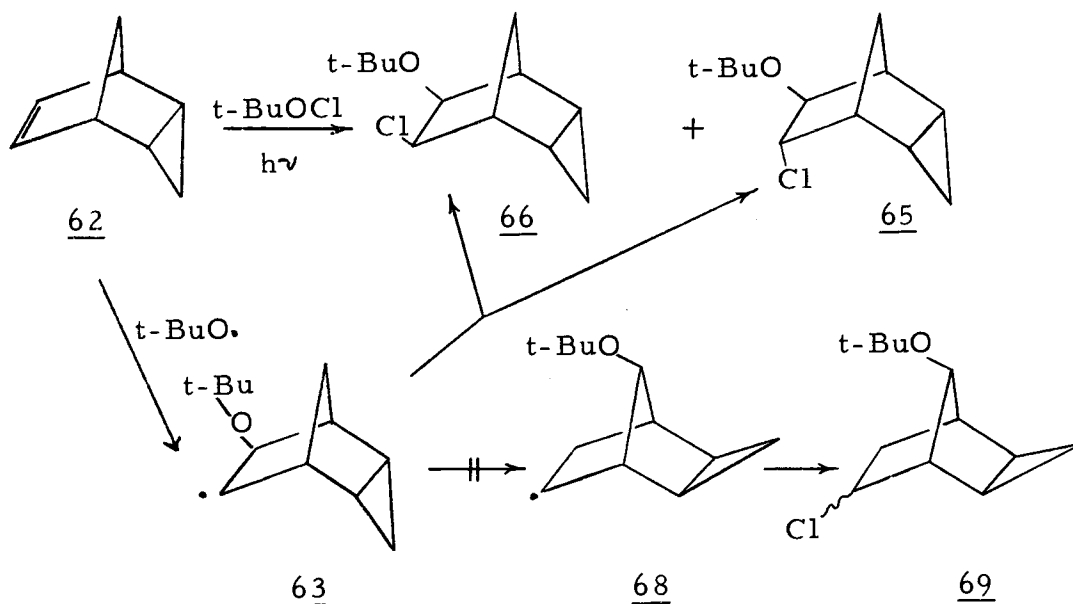
The behavior of the adduct radical is in striking contrast to that

of the carbonium ion. While the carbonium ion is observed to give

exclusively rearranged products in a stereospecific fashion (89), the

radical equivalent fails to display this tendency. A comparison with

the norbornene-t-butoxy adduct radical would be appropriate. The

latter yields the trans- and cis-adducts in the ratio 4:1 (57). The

predominance of the trans-adduct was explained as due to the steric

blocking of the exo-face by the t-butoxy group. In the present case,

in addition to the steric shielding of the exo-face by the t-butoxy

group, we also have the endo-cyclopropane ring blocking the endo-

face. These are apparently nearly evenly balanced, thus giving rise

to the observed product proportions. Finally it is to be observed

that the lack of stereospecific chain transfer coupled with the conspicu-

ous absence of skeletal rearrangements makes the representation of

the radical intermediate as a classical radical mandatory. The failure

of the olefin to evince abstraction at C_8 reveals that this process could

not compete with the fast addition pathway which leads to relief of

strain of a double bond in a rigid tricyclic system.

When the exo-olefin was irradiated with t-butylhypochlorite

in carbon tetrachloride at 40°, the products were found by vpc analy-

sis to be composed of two adducts in the ratio 78:22 in the order of

increasing retention times in a yield of 56%. These were identified

as the trans- and the cis-adducts on the basis of their spectral data.

The ir spectrum of the trans-adduct (Figure 21) showed bands

attributable to cyclopropane ring (3088 and 3032 cm^{-1}, both weak),

C-O stretching (1190, 1116, 1064, and 1030 cm^{-1}, all strong), and

C-Cl stretching (806 cm^{-1}, strong, and 755 cm^{-1}, medium). The

nmr spectrum (Figure 22, 100 MHz, CCl_4) had resonance signals at

τ 6.23 (doublet of a doublet, J = 2.9 Hz, 2.0 Hz, 1H, the α-chloro pro-

ton), 6.61 (triplet, J=2.0 Hz, 1H, the α-t-butoxy proton), 7.63 (unre-

solved multiplet, 1H, the bridgehead proton β to chlorine), 7.94 (sing-

let, 1H, the bridgehead proton β-t-butoxy), 8.5-8.9 (multiplets with a

large singlet at 8.86, 11 H, the anti-C_8 proton, and the C_4 proton)

9.08 (a poorly resolved multiplet of a doublet of the AB pattern,

J=12 Hz, 1 H, the syn-C_8 proton), 9.2-9.5 (multiplets, 2 H, the

C_2 proton and the syn-C_4 proton), and 9.65-9.92 (a four-peak signal

with a spacing of 7 Hz between each consecutive pair of peaks, 1 H,

the anti-C_3 proton). The ir spectrum of the cis-adduct (Figure 23)

showed characteristic bands at 3092 and 3032 cm^{-1} (cyclopropyl C-H

stretching), 1195, 1110, 1090, 1080 and 1030 cm^{-1} (C-O stretching),

and 745 and 712 cm^{-1} (C-Cl stretching). The nmr spectrum (Figure

24, 100 MHz, CCl_4) showed resonance signals at τ6.23 (doublet of a

doublet, J=6 Hz, 2.3 Hz, 1 H, the α-chloro proton), 6.51 (doublet

of a doublet, J-6 Hz, 1.9 Hz, 1 H, the α-t-butoxy proton), 7.69

(singlet, 1 H, the bridgehead proton β to chlorine), 7.96 (singlet,

1 H, the bridgehead proton β to t-butoxy), 8.55 (a doublet of the AB

pattern, J=11 Hz, 1 H, the anti-C_8 proton), 8.83 (a large singlet,

9 H, the t-butoxy proton), 9.25 (an unresolved multiplet of a doublet

of the AB pattern, J=11 Hz, 1 H, the syn-C_3 proton), and 9.7-9.9

(multiplet, 1 H, the anti-C_3 proton).

Both the trans- and the cis-adducts on reduction with TBTH

at 95° gave exclusively exo-6-t-butoxy-exo-tricyclo[3.2.1.0^{2,4}]-

octane 73. The ir spectrum of the sole product (Figure 25) showed

principal bands at 3092, and 3016 cm^{-1} (cyclopropyl C-H stretching),

and 1195, 1155, 1088, 1060 and 1025 cm^{-1} (C-O stretching). The

nmr spectrum (Figure 26, 100 MHz, CCl_4) had resonance signals

at τ6.54 (doublet of a doublet of a doublet, J=7.0 Hz, 3 Hz, 1 Hz, 1 H,

the α-butoxy proton), 7.87 (poorly resolved multiplet, 1 H, the

bridgehead proton β to t-butoxy), 7.95 (singlet, 1 H, the other

bridgehead proton), 8.35 (a doublet of a doublet of a doublet of the

AB pattern, J=12.5 Hz, 7.0 Hz, 2.2 Hz, 1 H, the endo-C_7 proton),

8.75 (triplet of a doublet, of the AB pattern, J=12.5 Hz, 3 Hz, 1 H,

the exo-C_7 proton), 8.86 (singlet, 9 H, the t-butoxy protons), 8.96

(a poorly resolved doublet of a doublet of the AB pattern, J=12 Hz,

1 H, the anti-C_8 proton), 9.28 (a poorly resolved multiplet of a

doublet of the AB pattern, J=12 Hz, 1 H, the syn-C_8 proton), 9.35-

9.6 (multiplet, 3 H, the C_2 and C_4 protons and the syn-C_3 proton)

and 9.85-10.09 (multiplet, 1 H, the anti-C_3 proton). The spectrum

showed a remarkable resemblance to that of exo-6-hydroxy-exo-

tricyclo[3.2.1.0^{2,4}]octane.
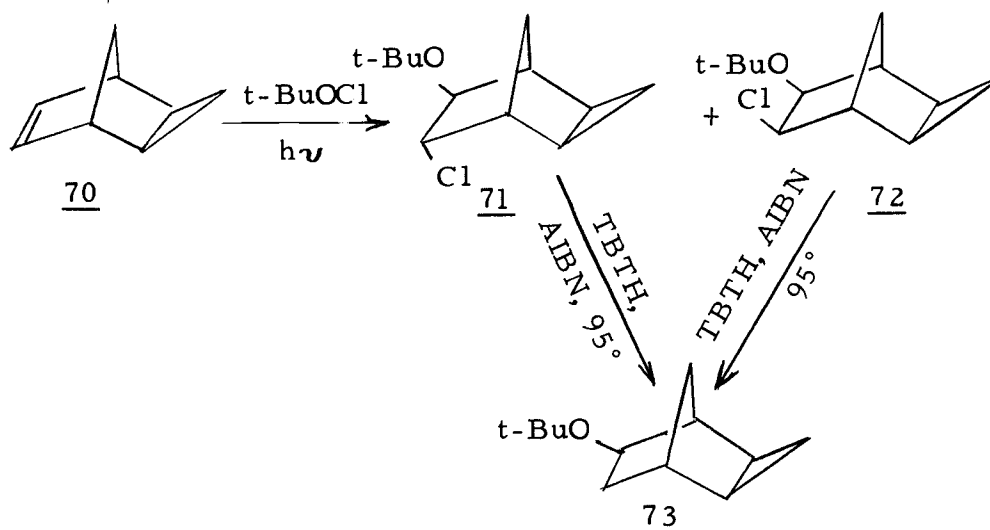
The results of the free radical addition study only lend further

support to the conclusion drawn from the abstraction study that a

single non-classical radical intermediate can be ruled out. Further,

in the present exo-tricyclooctene case the ratio of the trans:cis-

adducts is similar to the value found in the case of the norbornene-

t-butylhypochlorite adducts (5:1). No skeletal rearrangement of the

adduct radical was observed by us--a distinct contrast to the behavior

of the carbonium ion. Also significant is the absence of monochlor-

ides resulting from hydrogen abstraction.

No less different was the picture that emerged from the irradi-

ation of a solution of deltacyclene with t-butylhypochlorite under

conditions identical to those employed for the other olefins. The

products were found by vpc analysis to consist of two adducts, the

trans- and the cis-adducts in the ratio 85:15 in a yield of 37%. No

significant amounts of monochlorides ($\geq 2\%$ could have been detected)

were observable. Both the adducts gave satisfactory microanalytical

data. The ir spectrum of the trans-adduct showed the presence of

cyclopropane ring (a weak band at 3056 cm^{-1}), ether C-O linkage

(intense absorptions at 1185 1152, 1060, and 1021 cm^{-1}), and C-Cl

linkage (strong bands at 790 cm^{-1} and weak bands at 775 and 733

cm^{-1}), and a nortricyclene ring (a strong band at 800 cm^{-1}). The

nmr spectrum (100 MHz, CCl$_4$) showed signals at $\tau 6.07$ (doublet of

a doublet, J=4.0 Hz, 2.0 Hz, 1 H, the α-chloro proton), 6.24 (poorly

resolved doublet, J=2 Hz, 1 H, the α-t-butoxy proton), 7.8 (unre-

solved multiplet, 1 H, the bridgehead proton β to chlorine), 7.88

(unresolved multiplet, 1 H, the bridgehead proton β to t-butoxy), 8.15

(unresolved triplet, 1 H, the C_6 proton) 8.42 (singlet, 2 H, the C_5

protons) 8.74 (singlet, 2 H, the C_2 and C_3 protons), 8.82 (singlet,

9 H, t-butoxy protons), 9-9.15 (a doublet of a doublet of a doublet,

J=11 Hz, 6 Hz, 2 Hz, 1 H, the C_4 proton). The cis-adduct was con-

taminated to the extent of 32% by an unidentified, inseparable material.

The ir spectrum showed bands at 3056 cm^{-1} (weak, assignable to

cyclopropyl C-H stretching), 1185 and 1086 cm^{-1} (medium and strong

respectively, both assignable to C-O stretching), 800 cm^{-1} (strong,

assignable to nortricyclene ring), and 765 and 715 cm^{-1} (both weak,

assignable to C-Cl stretching). The nmr spectrum (100 MHz, CCl_4)

contained signals of τ5.9 (doublet J=6 Hz), 6.15 (doublet, J=6 Hz),

7.35 (poorly resolved multiplet), 7.64 (envelope), 7.88 (envelope),

8-8.3 (multiplets), 8.48 (a broad singlet), 8.52-8.98 (multiplets with

a large singlet, at 8.85), 9.05-9.22 (multiplet). Integration data

were misleading due to contamination of the sample. For the same

reason, assignment of most of the signals was rendered difficult.

Both the adducts on reduction with TBTH at 95° gave the

same product, exo-8-t-butoxydeltacyclane 77. The cis-adduct, in

addition to this ether, gave 32% of an unidentified product, probably

due to its contaminant. The elemental analysis of the reduction

product from both the adducts was satisfactory for the expected

$C_{13}H_{20}$ O formula. The ir spectrum showed the presence of cyclo-

propane ring (a weak band at 3056 cm^{-1}), and C-O linkage (strong

In this case also the absence of stereospecificity of the products and the lack of skeletal rearrangements are in marked contrast to the behavior of the cationic analog (30-32). The products can be satisfactorily accounted for entirely in terms of a classical radical whose direction of chain transfer is determined by steric factors. Another noteworthy feature is that even abstraction of a cyclopropyl carbinyl hydrogen is not able to compete with the addition pathway. This is perhaps the most eloquent testimony to the relief of strain that attends the formation of the adduct radical in these bridged polycyclic systems.

III. EXPERIMENTAL SECTION

All melting points were determined using a Büchi melting point apparatus and are corrected. All boiling points are uncorrected. Infrared spectra were recorded on a Beckman Model IR-8 Infrared Spectrophotometer. Nmr spectra were recorded on a Varian Associates A-60 or HA-100 Nmr Spectrometer. Mass spectra were recorded using an Atlas CH7 Mass Spectrometer. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Fritz-Pregl-Straße 14-16, West Germany, or Dornis U. Kolbe, 433 Mulheim a.d. Ruhr, Hohenweg 17, West Germany. Vpc analysis were carried out using an F and M Model 700 Chromatograph equipped with dual columns and thermal conductivity detectors or a Varian Aerograph series 1200 Chromatograph equipped with a flame ionization detector. The following columns were employed:

1. 32 ft. x 0.25 in. aluminum containing 20% Carbowax 20 M plus 2% XF-1150 on Anakrom 70-80 ABS.

2. 29 ft. x 0.25 in. aluminum containing 13% TCEP on 30-60 Chromosorb PAW.

3. 18 ft. x 0.25 in. aluminum containing 15% QF-1 on Anakrom 70-80 ABS.

4. 18 ft. x 0.125 in. stainless steel containing 10% UCW-98 (methyl

vinyl) on 80-100 Diatoport S.

5. 28 ft. x 0.25 in. aluminum containing 9% FFAP on Anakrom 70-80 ABS.

6. 7 ft. x 0.25 in. aluminum containing 9% FFAP on Anakrom 70-80 ABS.

7. 10 ft. x 0.25 in. aluminum containing 10% Carbowax 20 M on Anakrom 70-80 ABS.

8. 10 ft. x 0.25 in. aluminum containing 15% QF-1 on Anakrom 70-80 ABS.

9. 32 ft. x 0.125 in. copper containing 5% Carbowax 20 M plus 0.5% XF-1150 on 60-80 Firebrick.

10. 20 ft. x 0.375 in. aluminum containing 12% Carbowax 20 M on Anakrom 70-80 ABS.

11. 18 ft. x 0.25 in. aluminum containing 13% TCEP on 30-60 Chromosorb W.

12. 23 ft. x 0.25 in. aluminum containing 13% TCEP on 30-60 Chromosorb P.

13. 3.5 ft. x 0.25 in. aluminum containing 10% SE-30 on Anakrom 110-120 AS.

14. 20 ft. x 0.25 in. aluminum containing 15% DC-200 on Anakrom 70-80 ABS.

15. 12 ft. x 0.25 in. aluminum containing 13% TCEP on Chromosorb 30-60 PAW.

Product ratios and percentage yields calculated from chromatographic data are based on relative peak areas and are uncorrected for the variations of thermal conductivity with molecular weight. Glassware used in reactions requiring anhydrous conditions was previously dried at ca. 110° in a drying oven for several hours. Sodium methoxide used in tosylhydrazone decompositions was dried at 50-60° in vacuum (0.5 mm Hg) for several hours. Diglyme used in tosylhydrazone decompositions was initially dried over anhydrous calcium chloride and then over lithium aluminum hydride and then distilled repeatedly from the hydride until the infrared spectrum indicated total exclusion of moisture. All reported reaction temperatures must be regarded as approximate unless otherwise stated. All tosylhydrazones were dried in vacuum at elevated temperatures prior to their use in base-catalyzed decompositions.

<u>Preparation of 5, 5-Dimethoxy-1, 2, 3, 4-
tetrachlorocyclopentadiene</u>

The method of Newcomer and McBee (98) was used. Hexachloro-cyclopentadiene (158.8 g, 0.0476 mol) was dissolved in 500 ml of absolute methanol in a three-necked two-liter flask provided with a stirrer and a water condenser. Reagent grade potassium hydroxide (85.5 g, 1.52 mol) dissolved in 400 ml of absolute methanol was added through an addition funnel over a period of 2.5 hr. The mixture

was then stirred for a period of 6 hr. After dilution with 700 ml of distilled water, the mixture was transferred to a separatory funnel. The lower heavy yellow oil was separated, washed with 3 x 200 ml of water, dried $(MgSO_4)$ and filtered under suction, giving 111.5 g (0.422 mol, 72.6% yield) of the title compound ($>$ 95% pure by vpc), b.p. 55-57° /0.3 mm.

Reaction of 5, 5-Dimethoxy-1, 2, 3, 4-tetrachlorocyclopentadiene with Cyclopropene. A solution of the ketal (17 g, 0.064 mol) in 50 ml of ether was treated at 0° with a slight excess of cyclopropene (from 30 g of sodium amide (0.769 mol) and 58.9 g (0.77 mol) of allyl chloride) generated by the method of Closs and Krantz (67). Removal of the solid residue by filtration followed by removal of volatile materials by rotary evaporation gave 18.58 g (0.061 mol, 95% yield) of the Diels-Alder adduct as orange red crystals. Recrystallized from methanol-water, m.p. 68.5-69.5°, lit. (65, 66) 69.5-70°.

Dechlorination of 1, 5, 6, 7-Tetrachloro-8, 8-dimethoxy-endo-tricyclo[3. 2. 1. 0$^{2, 4}$]oct-6-ene with Lithium. The procedure described by Gassman and Pape (99) was followed with minor experimental modifications. The chlorinated ketal (20 g, 0.066 mol) was treated with 76.1 g (1.03 mol) of commercial anhydrous t-butanol and 500 ml of reagent grade tetrahydrofuran in a three-necked one liter flask provided with a nitrogen inlet, mechanical stirrer, a reflux condenser and a calcium chloride drying tube. The flask was cooled by an ice

bath and the solution stirred. Finely scissored lithium ribbon (11.4 g, 1.64 g. atom) was added and the stirring continued. In about 1 hr, a highly exothermic reaction began to occur (caution: the reaction may become uncontrollable if the flask is not cooled sufficiently in advance). After stirring for 2 hr, the ice bath was replaced by a heating mantle and the mixture was maintained at a gentle reflux for 18 hr. The flask was then cooled by an ice bath and the excess lithium destroyed by cautious addition of 200 ml of absolute methanol. The resulting mixture was poured into 2 l of ice-water, which resulted in a clear brown solution. Repeated ether extraction of this solution, followed by drying ($MgSO_4$) and removal of ether on a rotary evaporator, gave 8.22 g (74% yield) of pure 8,8-dimethoxy-endo-tricyclo-[3.2.1.0^{2,4}]octane.

Hydrolysis of 8,8-Dimethoxy-endo-tricyclo[3.2.1.0^{2,4}]octane. Following the procedure of Pincock and Haywood-Farmer (17) with minor experimental modifications, the saturated ketal (8.2 g, 0.049 mol) was treated with 62 ml of glacial acetic acid in a 250 ml flask provided with a magnetic stirrer and a reflux condenser. The flask was placed in an oil bath maintained at 70-80° for 30 hr. At the end of this period, the flask was cooled by an ice bath and diluted with 100 ml of pentane. After neutralization of the acetic acid by careful addition of a solution of 63.5 g of sodium hydroxide in 250 ml of water, the mixture was extracted with 5 x 100 ml of pentane. The combined

pentane extracts were washed repeatedly with water, dried $(MgSO_4)$

and stripped of pentane by rotary evaporation at room temperature,

giving 5. 15 g (86% yield) of the crude endo-ketone. The crude ketone

obtained thus was used without further purification in subsequent

experiments.

Preparation of endo-Tricyclo[3. 2. 1.0$^{2, 4}$]octan-8-one Tosyl-

hydrazone. The general procedure of Bamford and Stevens (100) was

adapted to the preparation of this tosylhydrazone. To 5. 15 g (0. 0422

mol) of the endo-ketone in a 100 ml flask, provided with a magnetic

stirrer and a reflux condenser, was added 45 ml of 95% ethanol,

followed by 7. 85 g (0. 0422 mol) of tosylhydrazine and 2 drops of

concentrated HCl. A white flocculent precipitate formed in about

5 min. The mixture was gently heated at reflux for 2. 5 hr. The flask

was then cooled to room temperature and the solid product filtered

and dried by suction, giving 7. 25 g. An additional 0. 3 g of the

product was obtained by refrigerating the filtrate overnight. The

total yield of the tosylhydrazone was 7. 55 g (0. 026 mol, 61. 6% yield).

Recrystallization from absolute ethanol gave the tosylhydrazone with

mp 172-173° dec., lit. (66), 172-173° dec. (from methanol), ir

(KBr pellet), 3200 cm^{-1} (m, N-H, stretching), 3080 (shoulder,

cyclopropyl C-H stretching), 3056 (shoulder, cyclopropyl C-H

stretching or aromatic C-H stretching), 3040 (medium, cyclopropyl

C-H stretching or aromatic C-H stretching), 1668 (m, aromatic C=C

stretching), 1582 (m, aromatic C-H stretching), 1160 (s, SO_2-N

stretching).

<u>Anal</u>. Calcd. for $C_{15}H_{18}N_2O_2S$: C, 62.05; H, 6.24. Found:

C, 61.96; H, 6.16.

Decomposition of <u>endo</u>-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosyl-

hydrazone in the Presence of Excess Sodium Methoxide. In a three-

necked 250 ml flask provided with a magnetic stirrer, a nitrogen

inlet, and a vigreaux column heated to 80° by means of a heating

tape, was placed 4.92 g (0.0911 mol) of dry sodium methoxide and

140 ml of anhydrous diglyme. The vigreaux column was connected

to two dry ice - 95% ethanol traps in series and then to a gas bubbler.

The flask was heated to 82° by an oil bath and the tosylhydrazone

(4.61 g, 0.0159 mol) was added. The temperature was then raised

to and maintained at 150-155° for 4.5 hr. At the end of this period,

the vigreaux column was washed with pentane and the washings were

added to the liquid collected in the traps. The pentane solution (<u>ca</u>.

35 ml) was washed repeatedly with water, dried ($MgSO_4$) and concen-

trated by distillation to about 1.3 g. Vpc analysis of this concentrate

(col 1, 125°, 80 ml/min) showed that this material consisted almost

exclusively of pentane.

The cloudy diglyme suspension in the pot was diluted with 200

ml of water and extracted with 5 x 50 ml of pentane. The combined

pentane extracts were washed with 3 x 80 ml of water and dried

$(MgSO_4)$. Near-complete removal of pentane by distillation using a

vigreaux column yielded 1.897 g of a pale yellow liquid. Vpc analysis

of this liquid under conditions identical to those used previously

revealed that the liquid consisted of, besides traces of pentane and

diglyme, 4 components in the ratio 4:33:11:51 in the order of increas-

ing retention times plus about 1% of unisolable products in a total

yield of approximately 80%.

The 4% component was identified as tricyclo[3.3.0.0^{4,6}]oct-2-

ene by comparison of its ir and nmr spectra with those of an authentic

sample obtained by Zirner and Winstein (68) and by Roth and Peltzer

(69).

The 33% component had vpc retention time, ir, nmr, and mass

spectra identical to those of an authentic sample of tetracyclo-

[3.3.0.0.^{2,8}0^{4,6}]octane, reported by Freeman, Kuper and Rao

(70, 33).

The 11% component was identified as <u>anti</u>-8-methoxy-<u>endo</u>-

tricyclo[3.2.1.0^{2,4}]octane on the basis of its spectral data: mass

spectrum: parent peak at m/e 138; ir (neat): 3090 cm^{-1} (w), 3030

(m) and 3010 (m) (all assignable to cyclopropyl C-H stretching), 1195

(s), 1120 (shoulder) and 1110 (s) (all assignable to C-O stretching);

nmr (100 MHz, CCl_4): τ 6.5 (unresolved triplet, 1H, the α-methoxy

proton), 6.85 (singlet, 3H, the methoxy protons) 7.8-8.0 (multiplet,

2H, the bridgehead protons), and 8.4-9.75 (complex multiplets, the

protons on C_6, C_7, C_2, C_4 and C_3). The structure assignment was confirmed by an independent synthesis of this compound.

<u>Anal</u>. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.02; H, 10.37.

The 51% component was identified as <u>endo</u>-2-methoxytricyclo-[3.3.0.0^{4,6}]octane on the basis of its spectral data and confirmation by an independent synthesis: mass spectrum, parent peak at m/e 138; ir (neat), 3035 cm^{-1} (s), assignable to cyclopropyl C-H stretching), 1115 (s) and 1097 (s) (assignable to C-O stretching); nmr (100 MHz, CCl_4), τ 6.1-6.55 (six-peak signal, 1H, the α-methoxy proton), 6.85 (singlet, 3H, the methoxy protons), and 7.3-9.1 (multiplets, 10 H, the remaining protons). The spectrum shows a striking similarity to those of <u>endo</u>-2-chloro- and <u>endo</u>-2-hydroxytricyclo-[3.3.0.0^{4,6}]octane.

<u>Anal</u>. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.15; H, 10.28.

<u>Lithium Aluminum Hydride Reduction of the <u>endo</u>-Ketone.</u>

Lithium aluminum hydride (3.5 g, 0.092 mol) was suspended in 40 ml of anhydrous ether in a three-necked 200 ml flask, provided with a reflux condenser and calcium chloride tube, an overhead mechanical stirrer and a pressure-compensated addition funnel. The flask was cooled by an ice bath and the contents stirred. A solution of the <u>endo</u>-ketone (4.5 g, 0.036 mol) in 20 ml of anhydrous ether was

added dropwise through the addition funnel to the stirred suspension.

On completion of the ketone addition, the ice bath was removed and

the flask was warmed externally by means of a heating mantle to

obtain a gentle reflux for about 15 hr. The flask was then cooled

by an ice bath and the excess hydride destroyed by cautious addition

of a saturated solution of ammonium chloride in water. Ether extrac-

tion, drying of the ether extracts ($MgSO_4$), and subsequent removal

of ether on a rotary evaporator gave 3.47 g (76% yield) of the syn-

and the anti-alcohols in the ratio 64:36 (Col 10, 140°, 230 ml/min)

as previously reported (17). The crude mixture of alcohols obtained

thus was used without further purification in subsequent reactions.

Preparation of syn- and anti-8-Methoxy-endo-tricyclo-

[3.2.1.0^{2,4}]octane. A mixture of the syn- and the anti-alcohols

(1.06 g, 0.0855 mol) in ether solution was added dropwise to a sus-

pension of sodium hydride (1.14 g, 0.0272 mol) in pentane, in a

nitrogen atmosphere, in a three-necked 150 ml flask provided with

a reflux condenser and calcium chloride tube, a pressure-compen-

sated addition funnel, a nitrogen inlet and a magnetic stirrer. When

the alcohol addition was complete, 9.39 g (0.0661 mol) of methyl

iodide was added and the mixture stirred for 16 hr. An additional

7.82 g (0.0552 mol) of methyl iodide was added about 13 hr after the

commencement of the reaction. Any unreacted sodium hydride was

destroyed by addition of anhydrous methanol. A clear yellow solution

resulted which was taken up in 40 ml of ether. The solution was repeatedly washed with water and then dried ($MgSO_4$). Removal of ether by rotary evaporation at room temperature gave 0.55 g (47% yield) of a yellow liquid. Vpc analysis (for conditions vide supra) revealed that this liquid consisted of two methyl ethers in the ratio 37:63 in the order of increasing retention times. The 37% ether had vpc retention time, ir, and nmr spectra identical to those of the 11% component of the tosylhydrazone decomposition products.

The 63% ether which must be the syn-ether gave spectral data consistent with the expected structure: ir (neat), 3095 (w), 3060 (w), 3030 (shoulder) (all assignable to cyclopropyl C-H stretching), 1209 (s), 1135 (s) and 1107 (s), all assignable to C-O stretching; nmr (100 MHz, CCl_4): τ 6.25 (unresolved triplet, 1H, the α-methoxy proton), 6.73 (singlet, 3H, the methoxy protons), 7.85 (unresolved triplet, 2H, the bridgehead protons), and 8.47-9.2 (complex multiplets, 8H, the remaining protons).

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.35.

Methanolysis of anti-8-Chloro-endo-tricyclo[3.2.1.0^{2,4}]-octane. The anti-chloride (0.31 g, 22 mmol) was treated with 3 ml of anhydrous methanol and 0.22 g (22 mmol) of anhydrous calcium carbonate in a 10 ml flask provided with a magnetic stirrer and a reflux condenser. The mixture was heated to reflux for 13 hr.

After cooling to room temperature, the solid residue was filtered

off and the filtrate subjected to vpc analysis (Col 1, 130°, 75 ml/min).

The solvolysis was not complete. The only solvolysis product that

was present had vpc retention time and ir spectrum identical to those

of endo-2-methoxytricyclo[3.3.0.0^{4,6}]octane obtained in the methoxide

ion-induced decomposition of the tosylhydrazone.

Study of the Effect of Added Methanol-O-d on the Composition

of the Products in the Decomposition of the endo-Ketone Tosyl-

hydrazone. Several runs were made in which the decomposition of

the tosylhydrazone was carried out at 145-150° in the presence of

different amounts of added methanol-O-d (83% d$_1$) and excess sodium

methoxide (0.44 g, 0.008149 mol), methanol-O-d (45.5 mg, 1.38

mmol) in 20 ml of anhydrous diglyme. The products were composed

of 2% of the rearranged olefin 9, 21% of the tetracyclic hydrocarbon

10, 14% of the endo-anti-ether 11, and 64% of the rearranged endo-

ether 12.

(ii) The tosylhydrazone (0.40 g, 0.001377 mol) was decomposed

with sodium methoxide (0.44 g, 8.2 mmol) and methanol-O-d (0.233

g, 7.06 mmol) in 20 ml of anhydrous diglyme. The products were

composed of 1% of the rearranged olefin, 9% of the tetracyclic hydro-

carbon, 13% of the endo-anti-ether, and 78% of the rearranged endo-

ether.

(iii) The tosylhydrazone (2 g, 7 mmol) was decomposed with

sodium methoxide (2.14 g, 39.6 mmol) and methanol-O-d (2.70 g.

81.8 mmol) in 100 ml of anhydrous diglyme. The products consisted

of 1% of the rearranged olefin, 7% of the tetracyclic hydrocarbon,

11% of the endo-anti-ether and 81% of the rearranged endo-ether.

(iv) The tosylhydrazone (0.1040 g, 0.358 mmol) was decom-

posed with sodium methoxide (0.1200 g, 2.2 mmol) and methanol-O-d

(0.9650 g, 29.2 mmol) in 7 ml of anhydrous diglyme. The products

were composed of 0% (< 1%) of the rearranged olefin, 3% of the tetra-

cyclic hydrocarbon, 16% of the endo-anti-ether, and 81% of the re-

arranged endo-ether.

Effect of Change of Methoxide Ion Concentration on the Relative

Proportions of the Products in the Decomposition of the Tosylhydra-

zone. Several runs were made in which the tosylhydrazone was

decomposed with varying amounts of sodium methoxide in diglyme

in a nitrogen atmosphere at 140-150° and the products worked up

and analyzed as above (Col 1).

(i) The tosylhydrazone (0.50 g, 1.7 mmol) was decomposed

with dry sodium methoxide (0.28 g, 5.2 mmol) in 30 ml of anhydrous

diglyme. The products consisted of 4% of the rearranged olefin 9,

32% of the tetracyclic hydrocarbon 10, 13% of the endo-anti ether 11,

and 51% of the rearranged endo-ether 12.

(ii) The tosylhydrazone (0.50 g, 1.7 mmol) was decomposed

with dry sodium methoxide (1.20 g, 2.2 mmol) in 30 ml of anhydrous

diglyme. The products were found to be composed of 4% of the rearranged olefin, 31% of the tetracyclic hydrocarbon, 12% of the endo-anti-ether and 53% of the rearranged endo-ether.

(iii) The tosylhydrazone (0.50 g, 1.7 mmol) was decomposed with dry sodium methoxide (1.68 g, 31.1 mmol) in 30 ml of anhydrous diglyme. The products were composed of 4% of the rearranged olefin, 32% of the tetracyclic hydrocarbon, 11% of the endo-anti-ether, and 52% of the rearranged endo-ether.

Preparation of Norbornan-7-one Tosylhydrazone. Norbornan-7-one (3.21 g, 0.0292 mol), prepared by the method of Gassman and Pape (99) was treated with tosylhydrazine (5.54 g, 29.8 mmol) and 50 ml of reagent grade methanol in a 100 ml flask, fitted with a magnetic stirrer, a reflux condenser and a calcium chloride tube. Three drops of concentrated HCl were added and the mixture refluxed gently for 6 hr. A clear, pale yellow solution resulted which on cooling to room temperature deposited white crystals (2.01 g), mp. 141-143°. The crystals were collected by filtration and the filtrate refrigerated overnight at which point an additional 1.83 g of the product crystallized from solution. The total yield of the tosyl-hydrazone was 3.83 g (13.8 mmol, 47% yield). Recrystallization from methanol gave material with mp. 146-148°, lit. (24) mp. 152-153° from methanol.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.40; H, 6.52. Found:

C, 60.27, H, 6.33.

Decomposition of Norbornan-7-one Tosylhydrazone. The tosyl-
hydrazone (0.555 g, 2 mmol) was decomposed with dry sodium meth-
oxide (0.6250 g, 116 mmol) in 30 ml of anhydrous diglyme at 150-
155° for 4.5 hr in a nitrogen atmosphere. The experimental set-up
was similar to that used previously in the case of endo-tricyclo-
[3.2.1.0^{2,4}]octan-8-one tosylhydrazone. Work-up in the usual
manner gave 0.46 g of a colorless liquid. Vpc analysis (Col 1,
125-130°, 68 ml/min) showed that the products were composed of
4 components in the ratio 6:38:4:51 in the order of increasing reten-
tion times in a total yield of 97%. The 6%, 38% and 4% components
were in the hydrocarbon region and were not identified further. The
51% component was identified as 7-methoxynorbornane by comparison
of its vpc retention time and ir spectrum with those of an authentic
sample, synthesized as described below.

Reduction of Norbornan-7-one with Lithium Aluminum Hydride.
To a stirred suspension of lithium aluminum hydride (1.00 g, 26
mmol) in 30 ml of anhydrous ether in a three-mecked 200 ml flask
provided with a magnetic stirrer, reflux condenser and a calcium
chloride tube, and a pressure-compensated addition funnel, was
added a solution of norbornan-7-one (1.19 g, 10.8 mmol) in 10 ml
of anhydrous ether over a period of 25 min. The mixture was stirred
at room temperature for 6 hr. At the end of this period, the excess

hydride was destroyed by cautious addition, with simultaneous cooling by an ice bath, of a saturated solution of ammonium chloride in water. The ether layer was decanted off and the aqueous layer extracted with 3 x 20 ml of ether. The ether extracts were combined and dried ($MgSO_4$). Removal of ether by distillation using a vigreaux column gave 0.81 g (7.2 mmol, 67% yield) of norbornan-7-ol. The crude alcohol obtained thus was used without further purification in the next step.

Treatment of Norbornan-7-ol with Sodium Hydride and Methyl Iodide. A sodium hydride dispersion (1g, 57.2% concentration) in mineral oil was washed repeatedly with anhydrous ether to rid it of mineral oil in a three-necked 200 ml flask provided with a magnetic stirrer, a reflux condenser and a calcium chloride tube, and a pressure-compensated addition funnel. To the sodium hydride, free of mineral oil, was added 20 ml of anhydrous ether, and the suspension stirred. A solution of norbornan-7-ol (0.52 g, 4.6 mmol) in 10 ml of anhydrous ether was added slowly, followed by 20 g (140 mmol) of methyl iodide. The mixture was stirred at room temperature for 14 hr. The excess sodium hydride was then destroyed by slow addition of 15 ml of anhydrous methanol. After addition of 20 ml of water the two-phase liquid mixture was transferred to a separatory funnel. The lower aqueous phase was discarded and the ether layer was washed repeatedly with water (5 x 20 ml) and dried ($CaCl_2$).

Removal of ether by distillation using a vigreaux column gave 0.5 g

(85% yield) of 7-methoxynorbornane; ir (neat), 1205 (s), 1185 (s),

1160 (m), 1145 (s), 1110 (s), 1100 (s) and 1000 (s) (all assignable to

C-O stretching); nmr (100 MHz, CCl_4): τ 6.55 (singlet, 1H, the

α-methoxy proton), 6.75 (singlet, 3H, the methoxy protons), 7.9

(unresolved multiplet, 2H, the bridgehead protons), 8.2 (unresolved

multiplet, 2H, the exo-protons on C_2 and C_3 syn to the methoxy

group), 8.45 (unresolved multiplet, 2H, the exo-protons on C_5 and

C_6 anti- to the methoxy group) and 8.8 (complex multiplet, 4H, the

endo-protons on C_2, C_3, C_5, and C_6).

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C,

76.43; H, 11.35.

Preparation of endo-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosyl-

hydrazone-N-d$_1$. The tosylhydrazone (4 g) was shaken mechanically

for 3 days with 20 ml of deuterium oxide (99.8% D_2O) and a catalytic

amount of sodium methoxide in a 100 ml flask. The tosylhydrazone

was then recovered by filtration and dried in vacuo (1.5 mm Hg, 60°

for 24 hr). Analysis by ir showed about 50-70% deuterium incorpora-

tion. Thereupon this partially deuterated tosylhydrazone (0.73 g)

was mixed with 0.40 g of the undeuterated sample and suspended

in 10 ml of methylene chloride in a 50 ml flask fitted with a tight-

fitting glass stopper and a magnetic stirrer. A trace of sodium

methoxide, 16 ml of D_2O, and 3 drops of Aliquat 336 (methyl

tricaprylyl ammonium chloride) were added. The flask was tightly

stoppered and the contents stirred for 14 hr. The stirring bar was

then removed and the flask shaken by hand for 2 hr. The tosylhydra-

zone was filtered off using a Buchner funnel with its mouth covered

by aluminum foil. Analysis by ir showed 70-80% deuterium incorpora-

tion. Resubmission of this sample to the above treatment followed by

drying in vacuo (0.2 mm Hg) at 80-100° for 24 hr gave the tosyl-

hydrazone which had its imino hydrogen replaced almost completely

by deuterium. The extent of deuteration was estimated to be $\geqslant 97\%$

by quantitative ir analysis.

Decomposition of endo-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosyl-

hydrazone-N-d$_1$ with Excess Sodium Methoxide. The deuterated tosyl-

hydrazone (0.3640 g, 1.25 mmol) was decomposed at 150-155° with

dry sodium methoxide (0.3940 g, 7.30 mmol) in 20 ml of anhydrous

diglyme for 4.5 hr in a nitrogen atmosphere. The experimental

set-up consisted of a three-necked 200 ml flask provided with a

nitrogen inlet, reflux condenser and a calcium chloride tube, and

a magnetic stirrer. Work-up in the usual manner (dilution with

water, extraction with pentane, thorough washing of the pentane

extracts with water, drying ($MgSO_4$) and near-complete removal of

pentane by distillation using a vigreaux column) gave a colorless

liquid which on vpc analysis (Col 9, 120°, 25 ml/min) was found to

consist of, besides pentane, the rearranged olefin (10%), the

tetracyclic hydrocarbon (81%), the endo-anti-ether (3%), and the

rearranged endo-ether (6%). No attempt was made to estimate the

yield of the products.

The tetracyclic hydrocarbon which was now the major product

was submitted to mass spectral analysis to estimate the deuterium

content. The M-1 peak was eliminated using a low ionizing potential

(14.8 meV) to enable the percentage of deuterium to be computed.

Three runs were made and the percentage of deuterium was calcu-

lated to be 26%, 22% and 21%. The average of the three determina-

tions was 23%. The calculation was based on the method of Biemann

(101).

Test for Deuterium Exchange of Tetracyclo$[3.3.0.0^{2,8}0^{4,6}]$-

octane. A pure sample of the title hydrocarbon (0.0780 g, 0.74 mmol)

was treated with sodium methoxide (0.20 g, 3.7 mmol), methanol-O-d

(99% d_1, 0.029 g, 0.88 mmol) and 4 ml of anhydrous diglyme in a

three-necked 25 ml flask, provided with a magnetic stirrer, a reflux

condenser and a calcium chloride tube. The flask was maintained

at 150-155° for 4.5 hr by means of an oil bath. After cooling to

room temperature, the mixture was diluted with 40 ml of water and

extracted with 4 x 20 ml of pentane. The combined pentane extracts

were washed with water repeatedly and dried $(MgSO_4)$. The solution

was then concentrated to about 0.5 ml by distillation using a vigreaux

column and submitted directly to mass spectral analysis. No

deuterium incorporation was detectable. The limit of detection was

about 2-3%. Also no detectable isomerization to the rearranged

olefin was observed by vpc and mass spectral analysis.

Preparation of exo-Tricyclo[3.2.1.0^{2,4}]octane. This compound

was prepared by the addition of methylene to norbornene by the

Simmons-Smith procedure (82). Cupric acetate (0.56 g, 3.1 mmol)

was dissolved in 56 ml of boiling glacial acetic acid in a 250 ml

Erlenmeyer flask. To the hot solution was added 34 g (0.52 mol)

of 30-mesh granular zinc and the flask swirled for 3 min. The acetic

acid was decanted off and the zinc-copper couple washed with 56 ml

of boiling glacial acetic followed by 3 x 60 ml of anhydrous ether. The

ether-moistened zinc-copper couple was transferred to a three-necked

500 ml flask, provided with a magnetic stirrer, an addition funnel and

a reflux condenser and a calcium chloride tube. About 150 ml of

anhydrous ether was added. A small quantity of the total amount

of methylene iodide was added and the mixture stirred and gently

warmed to reflux. To the refluxing mixture, a solution of 23 g

(0.245 mol) of norbornene and 106 g (0.396 mol) of methylene iodide

was added slowly over a period of 80 min. External warming was

discontinued on completion of the addition. The mixture was stirred

for a total period of 49 hr. The zinc-copper couple was then filtered

off and the clear ether solution washed with 100 ml of ice-cold 1 N

HCl followed by 3 x 100 ml of water, dried (MgSO$_4$) and relieved of

ether by distillation using a vigreaux column. Further distillation

afforded 10.52 g (0.0974 mol, 40% yield) of the title hydrocarbon.

Preparation of endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene. The

method of Closs and Krantz (67) was used. A solution of freshly

cracked and distilled cyclopentadiene (5.85 g, 88.7 mmol) in 30 ml

of pentane was treated at 0° with a slight excess of cyclopropene,

generated from sodium amide (35 g, 0.90 mol) and allyl chloride

(90 g, 1.18 mol). Filtration to remove a small amount of solid

residue, followed by removal of pentane by distillation using a

vigreaux column gave 7.41 g (79% yield) of endo-tricyclo[3.2.1.0$^{2\,4}$]-

oct-6-ene.

Hydrogenation of endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene. A solu-

tion of 15.05 g (0.1420 mol) of the endo-olefin in 170 ml of 95% ethanol

was treated with a pinch of 10% palladium on powdered charcoal in a

shaker bottle and placed in a Paar hydrogenation apparatus. The

hydrogen pressure was adjusted to 30 psi. In about 30 min the

hydrogenation was complete and the pressure dropped to and remained

steady at 16 psi. The bottle was removed and the mixture, after

removal of the catalyst by filtration, was transferred to a separatory

funnel, diluted with 400 ml of water and extracted repeatedly with

pentane. Drying of the pentane extracts ($MgSO_4$) followed by removal

of pentane by distillation gave 13.74 g (0.1273 mol, 90% yield) of the

saturated hydrocarbon.

Preparation of t-Butylhypochlorite. The method described by
Teeter and Bell (102) was followed with minor experimental modifica-
tions. To a solution of 25 g of sodium hydroxide in 140 ml of water,
was added 23. 15 g (0. 313 mol) of commercial t-butanol in 140 ml of
water in a three-necked 500 ml flask provided with a mechanical
stirrer, a gas inlet and a gas outlet. The flask was maintained at
10-15° by means of an ice water bath. Chlorine gas was rapidly
passed through the mixture for 0. 5 hr and then at a slow rate for
0. 5 hr. The upper golden yellow oily layer was separated, washed
with 3 x 45 ml of 10% sodium carbonate solution followed by 4 x 35 ml
of water, dried ($CaCl_2$) and distilled, yielding 24. 5 g (0. 226 mol, 72%
yield) of t-butylhypochlorite.

Preparation of Tri-n-butyltin Hydride (TBTH). The method
of Kuivila and Beumel (84) was used with minor experimental modi-
fications. To an ice bath-cooled suspension of 2. 20 g (0.058 mol)
of lithium aluminum hydride in 150 ml of anhydrous ether in a 500
ml three-necked flask provided with an overhead mechanical stirrer,
a pressure-compensated addition funnel, a reflux condenser and a
calcium chloride tube, was added dropwise a solution of tri-n-butyltin
chloride (15 g, 0.046 mol) in 60 ml of anhydrous ether over a period
of 75 min. A slow stream of nitrogen was admitted through the addi-
tion funnel all the time. On completion of the chloride addition, the
ice bath was removed and the mixture stirred at room temperature

for 8 hr. The excess hydride was destroyed by cautious, dropwise addition of water, with simultaneous cooling of the flask by an ice bath. The clear upper ether layer was decanted off, washed with ice-water (2 x 100 ml), dried (MgSO$_4$), and stripped of ether by distillation. On application of vacuum, a clear, colorless liquid which turned water-white after a few min distilled over, b.p. 90-91° /1.5-1.7 mm. The yield of the tin hydride was 9.57 g (0.0329 mol, 71.4%). The hydride was preserved in the refrigerator in a tightly stoppered flask, covered with aluminum foil to avoid exposure to light.

Photochlorination of exo-Tricyclo[3.2.1.0^{2,4}]octane with t-Butylhypochlorite. To a solution of 10.6 g (0.0931 mol) of the exo-hydrocarbon in 20 ml of reagent grade carbon tetrachloride in a 50 ml flask, provided with a magnetic stirrer and a reflux condenser, was added 5.05 g (0.0465 mol) of t-butylhypochlorite and the flask placed in a 40±2° oil bath. The solution was irradiated with a 300 watt Sylvania light bulb for 20 min from a distance of 1 in. The solution was stirred for an additional five min after discontinuance of irradiation. The solution, which was yellow to start with, was now colorless due to the color of the t-butylhypochlorite having been discharged. After partial removal of solvent by distillation, the products were analyzed by vpc (col 2, 135°, 75 ml/min) and found to be composed of four monochlorides in the ratio 4:17:67:12 in the order of increasing retention times in a total yield of 27%. No dichlorides were detectable by vpc. The 4% component was too small to permit its isolation and characterization. The other three components were isolated by vpc collection and each was found to show only one peak on rejection, thus indicating their

stability to interconversion on the column under the conditions of analysis.

The 67% component was identified as exo-6-chloro-exo-tricyclo-[3.2.1.0^{2,4}]octane on the basis of its spectral data and its identity was confirmed by comparison with an authentic sample synthesized by two independent methods: ir (neat), 3080 (w), 3020 (m) both assignable to cyclopropyl C-H stretching), assignable to cyclopropyl ring deformation), and 750 (m) and 733 (s) (both attributable to C-Cl stretching); nmr (100 MHz, CCl$_4$): τ 6.45 (triplet of a doublet, J = 6.5 Hz, 2.0 Hz, 1H, the α-chloro proton), 7.6 (envelope, 1H, the bridgehead proton), 8.05 (a doublet of a doublet of a doublet, J = 13 Hz, 7 Hz, 2.5 Hz, 1H, the endo-C$_7$ proton), 8.8 (doublet, J = 10.5 Hz, 1H, the anti-C$_8$ proton), 9.1 (multiplet of a doublet, J = 10.5 Hz, 1H, the syn-C$_8$ proton), 9.45 (complex multiplet, 3H the cyclopropyl protons on C$_2$, C$_4$, and the syn-C$_3$ proton) and 9.9 (multiplet, 1H, the anti-C$_3$ proton); mass spec: parent peaks at m/e 142 and 144.

Anal. Calcd. for C$_8$H$_{11}$Cl: C, 67.38; H, 7.78. Found: C, 67.36; H, 7.89.

The 12% component was assigned the structure endo-6-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane on the basis of its spectral data. This assignment was confirmed by an independent synthesis of this compound: ir (neat), 3105 (w), 3040 (m) (both assignable to cyclopropyl

C-H stretching), 1034 (m) (cyclopropane ring deformation), 757 (s) and 732 (m) (both assignable to C-Cl stretching); nmr (100 MHz, CCl_4): τ 5.88 (triplet of a doublet, J = 9 Hz, 3.5 Hz, 1H, the α-chloro proton), 7.55 (unresolved multiplet, 1H, the bridgehead proton β to chlorine), 7.71 (envelope, 1H, the remaining bridgehead proton), 7.95 (multiplet, 1H, the endo-C_7 proton), 8.53-8.8 (multiplet, 2H, the exo-C_7 proton and the cyclopropyl proton on C_4), 8.85-9.4 (multiplets, 3H, the cyclopropyl proton on C_2 and the C_8 protons), 9.6 (An overlapping pair of triplets, J = 3 Hz, 1H, the syn-C_3 proton) and 9.94 (quartet, J = 7 Hz, 1H, the anti-C_3 proton); mass spec, parent peaks at m/e 142 and 144.

Anal. Calcd. for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.19; H, 7.78.

The 17% component was identified as 1-chloro-exo-tricyclo-$[3.2.1.0^{2,4}]$octane on the basis of its spectral data: ir (neat): 3100 (w), 3030 (w) (both assignable to cyclopropyl C-H stretching), 1035 (w), 1000 (s) (both assignable to cyclopropane ring deformation), and 733 (s) assignable to C-Cl stretching); nmr (100 MHz, CCl_4): τ 7.84 (unresolved multiplet, 1H, the bridgehead proton), 8.1-8.60 (complex overlapping multiplets, 4H, the exo- and the endo-protons on C_6 and C_7), 8.67 (doublet J = 11 Hz, 1H, the anti-C_8 proton), 8.89 (doublet, J = 11 Hz, 1H, the syn-C_8 proton), 8.90-9.24 (complex multiplets, 2H, the C_2 and C_4 protons), 9.37 (a five-peak signal with a spacing

of 3 Hz between each pair of peaks, 1H, the syn-C$_3$ proton) and

9.87 (a four-peak signal with a spacing of 7 Hz between each pair

of peaks, 1H, the anti-C$_3$ proton); mass spec, parent peaks at m/e

142 and 144.

Anal. Calcd. for C$_8$H$_{11}$Cl: C, 67.38; H, 7.78. Found: C,

67.20; H, 7.90.

Test for Stability of exo-6-Chloro-exo-tricyclo[3.2.1.0^{2,4}]-

octane to the Photochlorination Conditions. A pure sample of the

title chloride (0.0385 g, 0.271 mmol) was treated with t-butanol

(0.117 g, 1.58 mmol), acetone (40 μl), and carbon tetrachloride

(50 μl) and irradiated at 40° for 20 min. Analysis by vpc (col 3,

140°, 60 ml/min) and ir revealed that the starting chloride had not

suffered any detectable change.

Addition of Hydrogen Chloride to exo-Tricyclo[3.2.1.0^{2,4}]-

oct-6-ene. Hydrogen chloride gas was passed in a slow, steady

stream through a solution of the exo-olefin (1.49 g, 0.014 mol) in

6 ml of methylene chloride for 20 min. After removal of the solvent

by rotary evaporation at room temperature, the products were

analyzed by vpc (col 15, 115-120°, 60 ml/min). Monochlorides

accounting for 54% of the mixture were found to be present in a yield

of 33%. The monochloride fraction consisted of two components in

the ratio 48:52. The 52% component was the expected exo-6-chloro-

exo-tricyclo[3.2.1.0^{2,4}]octane and was identical to the 67% component

of the photochlorination products as observed by comparison of ir and

nmr spectra. The 48% component was an olefinic chloride and was

not completely characterized.

Reaction of exo-6-Hydroxy-exo-tricyclo[3. 2. 1. 0^{2,4}]octane

with Triphenylphosphine and Carbon Tetrachloride. The alcohol

(0.0920 g, 0.74 mmol) was stirred with triphenylphosphine (0.273 g,

1.04 mmol) and carbon tetrachloride (3 ml) in a tightly-stoppered

flask for 24 hr. After removal of solvent and any volatile materials

at reduced pressure (2 mm), the phosphorane ester was pyrolyzed

at 90-130° at 2.0 mm and the pyrolysate collected in a receiver

cooled by a bath of dry ice. Analysis of the pyrolysate (0.033 g)

by vpc (col 2, 150°, 60 ml/min) showed that the products were com-

posed of four components in the ratio 3:15:64:18 in a yield of 31%.

The 3% component was too small to permit its collection and identi-

fication.

The 64% and 18% components were the expected exo- and endo-

6-chlorides and were identical respectively to the 67% and 12% com-

ponents of the photochlorination products from exo-tricyclo-

[3. 2. 1. 0^{2,4}]octane. The 15% component was identified as nortri-

cyclylmethyl chloride on the basis of its spectral data: mass spec,

parent peaks at m/e 142 and 144; ir (neat), 3080 (s)(cyclopropyl C-H

stretching), 800 (s) (nortricyclene ring) and 730 (s) (C-Cl stretching);

nmr (100 MHz, CCl$_4$): τ 6.74 (complex multiplet, 2H, the

α-chloroprotons), 8.05 (unresolved multiplet, 1H, the bridgehead

proton on the carbon γ to chlorine), 8.18 (complex multiplet, 1H,

the β-chloro proton) and 8.5-9.5 (complex multiplets, 7 H, the

remaining protons).

Anal. Calcd. for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C,

67.53; H, 7.96.

Reduction of the Photochlorination Products with TBTH. A

mixture of the three monochlorides from the photochlorination of

exo-tricyclo[3.2.1.0^{2,4}]octane was isolated by vpc collection (0.0880

g, 0.62 mmol) and treated with TBTH (ca. 170 μl, 0.1860 g, 0.64

mmol) and cyclohexane (80 μl) in a small tube. Approximately 20 μl

was removed for later analysis as starting material. Two crystals

of AIBN were added and the tube sealed and placed in a 95±2° oil bath

for 24 hr. Vpc analysis (col 3, 145°, 46 ml/min) showed the pres-

ence of only one hydrocarbon product in a yield of 60% (versus cyclo-

hexane internal standard). The hydrocarbon was identified as exo-

tricyclo[3.2.1.0^{2,4}]octane by comparison of its vpc retention time,

ir, and nmr spectra with those of an authentic sample.

Reduction of 1-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane with

TBTH. About 8 μl of the chloride (0.0090 g, 0.063 mmol) was re-

duced with TBTH (0.0310 g, 0.107 mmol). About 8 μl of cyclo-

hexane was added. About 3 μl was withdrawn for later analysis.

A crystal of AIBN was added and the tube sealed and placed in

125-130° bath for 48 hr. After cooling to room tempera-

ture, the tube was opened and the contents analyzed by vpc

(Col 3) and mass spectroscopy. The sole hydrocarbon product had

vpc retention time and mass spectrum identical to those of an authen-

tic sample of exo-tricyclo[3. 2. 1. 0$^{2, 4}$]octane.

Photochlorination of endo-Tricyclo[3. 2. 1. 0$^{2, 4}$]octane with

t-Butylhypochlorite. A 1.56 molal solution of the endo-hydrocarbon

in carbon tetrachloride (22. 4 g of solution) was treated with t-butyl-

hypochlorite (1. 43 g, 0. 0132 mol, 0. 68 m) in a 50 ml flask provided

with a magnetic stirrer and a reflux condenser. The flask was placed

in an oil bath maintained at 40±2° and irradiated for 20 min with a

300 watt Sylvania light bulb from a distance of 1 in. The solution

was stirred for five more min after discontinuance of irradiation.

The solution became colorless due to the color of the t-butylhypo-

chlorite having been discharged. After partial removal of solvent

at reduced pressure, the products were analyzed by vpc (Col 2, 120°,

55 ml/min). Three peaks were seen in the monochloro region, the

first two being poorly separated from each other and the last one

being well separated from the first two. The first two peaks and the

last peak were in the ratio 95:5. Nmr analysis (100 MHz, CCl$_4$) in

the α-chloro region of the first two peaks collected together showed

that this was actually a mixture of three chlorides in the ratio 69. 4:

28.4:2.2. So the final analysis was that the photochlorination products

consisted of four monochlorides in the ratio 66:27:2:5, estimated to

be formed in a total yield of 33%. The 2% component did not lend

itself to isolation and characterization.

The 66% component was isolated by repeated vpc collection and identified as anti-8-chloro-endo-tricyclo[3.2.1.0^{2,4}]octane on the basis of its spectral data: ir (neat), 3088 (w), 3040 (w), 3020 (w) (all assignable to cyclopropyl C-H stretching), 785 (m), 760 (s), and 732 (m) (all assignable to C-Cl stretching; nmr (100 MHz, CCl$_4$), τ 6.28 (complex multiplet, 1H, the α-chloro proton), 7.63 (unresolved multiplet, 2H, the bridgehead protons), 7.86-8.13 (complex multiplet, 2H, the exo-protons on C$_6$ and C$_7$), 8.19-8.42 (complex multiplet, 2H, the endo-protons on C$_6$ and C$_7$), 8.51-8.67 (complex multiplet, 2H, the two cyclopropyl methine protons) and 9.17-9.37 (complex multiplet, 2H, the cyclopropyl methylene protons); mass spec, parent peaks at m/e 142 and 144. The structure assignment was confirmed by the stereospecific methanolysis of this chloride to endo-2-methoxy-tricyclo[3.3.0.0^{4,6}]octane.

Anal. Calcd. for C$_8$H$_{11}$Cl: C, 67.38; H, 7.78. Found: C, 67.22; H, 7.92.

The 27% component was identified as the rearranged endo-chloride, endo-2-chlorotricyclo[3.3.0.0^{4,6}]octane 16, by comparison of its ir and nmr spectra with those of an authentic sample supplied by Tanida (71).

Anal. Calcd. for C$_8$H$_{11}$Cl: C, 67.38; H, 7.78. Found: C, 67.58; H, 7.88.

The 5% component was not completely characterized. Its spectral data, however, showed that it could not be the rearranged exo-chloride, the endo-syn-8 chloride, the endo-syn-3-chloride, the endo-anti-3-chloride or the exo- or endo-6-chloride; ir (neat), 3120 (w), 3050 (m) (both assignable to cyclopropyl C-H stretching), 783 (s), 772 (s) and 725 (s) (all assignable to C-Cl stretching); nmr (100 MHz, CCl_4), τ 5.95 (triplet of a doublet, J = 11 Hz, 4 Hz, finer splitting of each of the lines to about 1 Hz was also observable, 1H), 7.52 (envelope, 1 H), 7.66 (envelope, 1H), 7.8-8.03 (complex multiplet, 2H), 8.05-8.23 (complex multiplet, 2H), 8.28-8.83 (complex multiplet, 3H), and 8.88-9.13 (doublet of a quartet, J = 6.5 Hz, 2 Hz, 1H); mass spec, parent peaks at m/e 142 and 144.

Anal. Calcd. for $C_8H_{11}Cl$: C, 67.38; H, 7.78. Found: C, 67.48; H, 7.67.

Test for the Stability of the endo-anti-8-Chloride 17 to the Reaction Conditions. A pure sample of the anti-chloride (0.0245 g, 0.172 mmol) was treated with anhydrous t-butanol (0.059 g, 0.798 mmol), reagent grade acetone (25 μl) and carbon tetrachloride (36 μl) in a 10 ml flask provided with a magnetic stirrer and a reflux condenser and a calcium chloride tube. The flask was placed in a 40±2° oil bath and irradiated for 20 min with a 300 watt Sylvania light bulb from a distance of 1 in. Vpc analysis (Col 2, 130°, 50-55 ml/min) showed only one monochloride peak, identical in retention time and

nmr (100 MHz, CCl_4) spectrum to that of the starting <u>anti</u>-chloride.

Test for the Homogeneity of the <u>endo</u>-<u>anti</u>-8-Chloride 17 by Vpc.

Pure samples of the <u>anti</u>-chloride were injected into several vpc

columns of divergent polarity (Col 1-5).   Only one peak was seen

in each case.   No detectable isomerization was observed on any of

the columns tried.

Test for Stability of the Rearranged <u>endo</u>-Chloride <u>16</u> to the

Photochlorination Conditions.   A pure sample of the title chloride

(0.0190 g, 0.134 mmol) was treated with t-butanol (0.0880 g, 1.19

mmol), acetone (30 μl), and carbon tetrachloride (40 μl) and irradi-

ated at 40° for 20 min by means of a 300 watt Sylvania light bulb.

After cooling to room temperature, the mixture was analyzed by

vpc (col 3, 140°, 60 ml/min).   There was only one monochloride

peak which was found to have retention time and ir spectrum identical

to those of the starting chloride.

Effect of Changing the Concentration of t-butylhypochlorite on

the Relative Proportions of the Monochlorides.

1) A 1.56 molal solution of the <u>endo</u>-hydrocarbon in carbon

tetrachloride (22.74 g of solution) was treated with t-butylhypochlorite

(1.03 g, 0.49 m) and irradiated for 20 min with a 300 watt Sylvania

light bulb at 40 ± 2° .   After removal of most of the solvent at reduced

pressure, the products were analyzed by vpc (col 2, 130° , 50-55 ml/

min) and nmr (100 MHz, CCl_4).   The monochlorides were composed

of 63% of the endo-anti-8-chloride, 28% of the rearranged endo-chloride, 6% of the incompletely characterized chloride, and 3% of the unidentified chloride.

2) A 1.56 molal solution of the endo-hydrocarbon in carbon tetrachloride was treated with t-butylhypochlorite (0.55 g, molality = 0.26) and irradiated for 20 min at 40±2°. Analysis of the products (vpc and nmr) showed that the monochlorides were composed of 32% of the endo-anti-8-chloride, 41% of the rearranged endo-chloride, 11% of the incompletely characterized chloride, and 16% of the unidentified chloride.

3) The endo-hydrocarbon (1.71 g, 0.0158 mol) in 21.7 g of carbon tetrachloride (molality of hydrocarbon = 0.73) was treated with t-butylhypochlorite (0.42 g, 0.00387 mol, molality = 0.18) and irradiated at 40±2° for 20 min. Analysis as above showed that the monochlorides were composed of 11% of the endo-anti-8-chloride, 56% of the rearranged endo-chloride, 15% of the incompletely characterized component, and 18% of the unidentified component.

Reaction of a Mixture of the endo-syn-8- and endo-anti-8-ols 14 with Thionyl Chloride in Ether. A 64:36 mixture of the endo-syn-8-ol and the endo-anti-8-ol 14 (2.94 g, 0.0237 mol) in 16 ml of anhydrous ether was treated with thionyl chloride (16.7 g, 0.14 mol) in 25 ml of anhydrous ether in a three-necked 50 ml flask provided with a magnetic stirrer, a reflux condenser and a calcium chloride

tube. The mixture was stirred and heated at reflux for 14 hr.

Unreacted thionyl chloride was removed by rotary evaporation.

70 ml of water was added and the mixture extracted repeatedly with

ether. The combined ether extracts were dried ($MgSO_4$) and the

ether evaporated, yielding 2.71 g (80% yield) of a brown liquid which

showed only one peak on vpc analysis (col 2, 140°, 100 ml/min).

The sole product was collected and identified as the rearranged

endo-chloride 16 by comparison of its vpc retention time and ir

spectrum to those of an authentic sample.

Reaction of a Mixture of the endo-syn-8- and the endo-anti-

8-ols 14 with Thionyl Chloride and Pyridine. A 64:36 mixture of

the endo-syn- and the endo-anti-alcohols 14 (1.725 g, 0.0139 mol)

was treated with anhydrous pyridine (1.225 g, 0.0155 mol) and

thionyl chloride (2.18 g, 0.0183 mol) in a 50 ml flask provided with

a magnetic stirrer and a reflux condenser and a calcium chloride

tube. The flask was cooled by an ice bath during the addition of

thionyl chloride. A dark brown semi-solid material formed almost

immediately. The ice bath was then replaced by an oil bath and the

temperature maintained at ca. 60° for 1.5 hr. The flask was then

placed in a 40° bath and connected to an aspirator to remove unreacted

thionyl chloride. 50 ml of water was added, with simultaneous cooling

by an ice bath, and a dark brown liquid resulted. Extraction with

5 x 30 ml of ether, drying of the combined ether extracts ($MgSO_4$)

and removal of ether by rotary evaporation at 40-50° gave 1.27 g

(64% yield) of a dark brown liquid which showed only one peak on vpc

analysis (col 2, 125-130°, 55 ml/min and col 1, 135°, 75 ml/min).

The sole peak was collected and identified as the rearranged endo-

chloride 16 by comparison of ir and nmr spectra with those of an

authentic sample.

Reaction of the endo-syn-8-ol 14a with Triphenylphosphine and

Carbon Tetrachloride. The endo-syn-8-ol (0.94 g, 7.5 mmol) was

treated with triphenylphosphine (2.08 g, 7.94 mmol) and carbon

tetrachloride (6 ml) in a 50 ml flask fitted with a magnetic stirrer

and a tight-fitting glass stopper. The mixture was stirred in the

closed flask for 24 hr at room temperature. After removal of solvent

at reduced pressure (20 mm), the phosphorane ester was pyrolyzed at

140-150° at 1-2 mm Hg pressure and the pyrolysate collected in a

receiver cooled by a bath of dry ice. The pyrolysate, 0.56 g of a

pale yellow liquid, on vpc analysis (col 2, 130-135°, 86 ml/min) was

found to consist chiefly of two components in the ratio 32:48 in the

order of increasing retention times in a yield of 41%. The remainder

consisted of about five unidentified, minor peaks.

The 32% component was identified as the rearranged endo-

chloride 16 by comparison of its vpc retention time, ir and nmr

spectra with those of an authentic sample.

The 48% component was identified as Δ^4-cycloheptenyl carbox-aldehyde on the basis of its spectral data and its reduction with lithium aluminum hydride to Δ^4-cycloheptenylmethyl alcohol. The spectral data for the aldehyde component are: ir (neat), 3029 (m) (assignable to olefinic C-H stretching), 1640 (w) (C=C bond), 2719 (m) (characteristic of aldehydic C-H stretching) and 1716 (s) (C=O stretching); nmr (100 MHz, CCl_4), τ 0.45 (singlet, 1H, the aldehydic proton), 4.3 (unresolved triplet, 2H, the olefinic protons), and 7.4-8.8 (complex multiplets, 9H, the remaining protons).

<u>Anal</u>. Calcd. for $C_8H_{12}O$: C, 77.38; H, 9.75. Found: C, 77.20; H, 9.91.

<u>Reduction of Δ^4-cycloheptenyl carboxaldehyde with Lithium Aluminum Hydride</u>. To a suspension of lithium aluminum hydride (0.04 g, 1.06 mmol) in 1 ml of anhydrous ether, was added slowly a solution of the aldehyde (0.0210 g, 0.17 mmol) in 1 ml of anhydrous ether and the mixture stirred for 4 hr. The excess hydride was destroyed by cautious addition of a saturated solution of ammonium chloride in water. Ether extraction, drying of the ether extracts ($MgSO_4$) and removal of ether by rotary evaporation gave 0.0140 g (66% yield) of Δ^4-cycloheptenylmethyl alcohol, identified by comparison of its vpc retention time (col 3), ir and nmr spectra with those of an authentic sample, supplied by Schick (94).

Reaction of the endo-anti-Alcohol with Triphenylphosphine and

Carbon Tetrachloride. The reaction of the anti-alcohol with carbon

tetrachloride ((4.1 ml) (0.67 g, 5.4 mmol) and triphenylphosphine

(1.50 g, 5.73 mmol) was carried out and the products analyzed under

conditions identical to those employed in the case of the syn-alcohol.

The products were found to be composed of the rearranged endo-

chloride (55%) and Δ^4-cycloheptenyl carboxaldehyde (45%) in a yield

of 39%.

Test for the Stability of the endo-anti-Chloride 17 to the

Triphenylphosphine, Carbon Tetrachloride Reaction Conditions.

A sample of the endo-anti-chloride (ca. 10 µl, 0.0113 g, 0.0796

mmol) was treated in an nmr tube with carbon tetrachloride (150 µl),

tetramethyl silane (ca. 2 µl), triphenylphosphine oxide (0.0385 g,

0.139 mmol), triphenylphosphine (0.0300 g, 0.115 mmol) and chloro-

form (15 µl). The tube was then cooled in a bath of acetone-dry ice

and sealed. After allowing the tube to stand at room temperature

for 24 hr, it was placed in an oil bath maintained at 140-150° for

1 hr. After cooling to room temperature, the mixture was analyzed

by 100 MHz nmr. There was no change in the spectrum of the endo-

anti-chloride. No detectable isomerization or rearrangement was

observed (>1% could have been detected).

Test for the Stability of the Rearranged endo-Chloride 16 to

Heat. A pure sample of the rearranged endo-chloride (ca. 10 µl) was

placed in a small glass tube and the tube sealed and placed in a 200-210° oil bath for 1 hr. After cooling to room temperature, the chloride was analyzed by 100 MHz nmr. There was no detectable isomerization of the chloride ($>$ 1% could have been detected).

Attempted Epimerization of the Rearranged endo-Chloride 16 to the Rearranged exo-Chloride 43. A pure sample of the rearranged endo-chloride 16 (0.77 g, 5.4 mmol) was treated with a solution of 5 g of lithium chloride in 35 ml of anhydrous dimethylformamide (the inorganic chloride took several hours to go into solution completely at room temperature) in a 50 ml flask provided with a magnetic stirrer and a reflux condenser and a calcium chloride tube. The flask was placed in an oil bath at 85-90° and the contents stirred for 39 hr. The flask was then allowed to cool to room temperature and the mixture diluted with 100 ml of water. Repeated ether extraction, washing of the ether extracts with water, followed by drying ($MgSO_4$) and removal of ether by rotary evaporation yielded 0.45 g of a brown liquid which was found by vpc (col 3), ir, and nmr analysis to consist almost exclusively of the starting endo-chloride. This represents a 58% recovery.

Reduction of the Rearranged endo-Chloride 16 with TBTH. A pure sample of the rearranged endo-chloride (0.073 g, 0.51 mmol) was treated with TBTH (0.1560 g, 0.536 mmol) and ca. 50 µl of cyclohexane in a small tube. Approximately 5 µl was removed for

later analysis. A crystal of AIBN was added and the tube sealed and placed in a 95±2° oil bath for 12 hr. After cooling to room temperature, the tube was opened and analyzed by vpc (col 3, 125°, 50 ml/min). There was only one hydrocarbon product, formed in a yield of 65% (versus cyclohexane internal standard). The vpc retention time, ir and nmr spectra of this sole hydrocarbon product were identical to those of an authentic sample of tricyclo[3.3.0.0^{4,6}]-octane.

Reaction of endo-Tricyclo[3.2.1.0^{2,4}]octan-8-one with Phosphorus Pentachloride. The procedure described by Jacobs (96) was followed with minor experimental modifications. A sample of the endo-ketone (1.23 g, 0.01 mol) in 5 ml of carbon tetrachloride was treated with 2.86 g (0.0137 mol) of phosphorus pentachloride in a 25 ml flask provided with a magnetic stirrer and a reflux condenser and a calcium chloride tube. The mixture was maintained at a gentle reflux and stirred for 4.5 hr. The flask was then cooled to room temperature and stripped of volatile materials at reduced pressure (36 mm), leaving a yellow semi-solid material. This material was stirred with pentane (17 ml) and filtered. The clear filtrate was washed with water repeatedly, dried (MgSO$_4$) and stripped of pentane by rotary evaporation at room temperature, giving 1.07 g of a yellow oil which on vpc analysis (col 12, 130-135°, 26 ml/min, col 13, 100°, 40 ml/min) showed only one peak which was collected and identified

as <u>endo</u>-2-chloro-5-chlorotricyclo[3.3.0.0^{4,6}]octane on the basis

of its spectral data: ir (neat), 3048 (w), 3016 (shoulder) (both assign-

able to cyclopropyl C-H stretching), and 820 (s), 812 (s) and 750 (s)

(all three assignable to C-Cl stretching); nmr (100 MHz, CCl_4): 5.48-

5.73 (six-peak signal, 1H, the α-chloroproton) and 7.05-8.7 (complex

multiplets, 9H, the remaining protons).

<u>Anal</u>. Calcd. for $C_8H_{10}Cl_2$: C, 54.24; H, 5.70. Found: C,

54.29; H, 5.73.

Reduction of <u>endo</u>-2-Chloro-5-chlorotricyclo[3.3.0.0$^{4\ 6}$]octane

<u>with TBTH</u>. A pure sample of the title dichloride (<u>ca</u>. 180 μl, 0.2260

g, 1.28 mmol) was treated with TBTH (<u>ca</u>. 750 μl, 0.8450 g, 2.91

mmol) and cyclohexane (<u>ca</u>. 200 μl) in a small tube. About 10 μl was

removed for later analysis. After addition of two crystals of AIBN,

the tube was sealed and placed in a 95±2° bath for 12 hr. After cool-

ing to room temperature, the tube was opened and the contents ana-

lyzed by vpc (col 3, 137°, 100 ml/min). Three products were found

to be present in the ratio 10:83:7 in the order of increasing retention

times in a yield of 84% (versus cyclohexane internal standard). The

10% component was identified as tricyclo[3.3.0.0^{4,6}]octane by com-

parison of ir and nmr spectra with those of an authentic sample. The

7% product was identified as the rearranged <u>endo</u>-chloride by com-

parison of its vpc retention time and ir spectrum with those of an

authentic sample.

The 83% component was identified as 5-chlorotricyclo-[3.3.0.0^{4,6}]octane on the basis of its spectral data: ir (neat), 3040 (m) (cyclopropyl C-H stretching), and 800 (m) and 765 (m) (both assignable to C-Cl stretching); nmr (100 MHz, CCl$_4$), 7.25 (triplet, 1H), the bridgehead proton on C$_1$, 7.65-8.05 (multiplet, 4H, the exo-protons on C$_2$, C$_3$, C$_7$, and C$_8$), 8.2 (doublet, 2H, the cyclopropyl protons on C$_4$ and C$_5$) and 8.45-8.9 (complex multiplets, 4H, the endo-protons on C$_2$, C$_3$, C$_7$, and C$_8$); mass spec, parent peaks at m/e 142 and 144.

Anal. Calcd. for C$_8$H$_{11}$Cl: C, 67.38; H, 7.78. Found: C, 67.44; H, 7.68.

Reaction of exo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene with t-Butyl-hypochlorite. The title olefin (1.40 g, 13.2 mmol) was dissolved in 4 ml of carbon tetrachloride in a flask provided with a reflux condenser, a drying tube and a magnetic stirrer. The flask was covered with aluminum foil to avoid exposure to light. After addition of t-butyl hypochlorite (0.71 g, 6.5 mmol), the foil was removed and the flask placed in a 40±2° bath and irradiated for 20 min with a 300 watt Sylvania light bulb from a distance of 1 in. After partial removal of volatile components at reduced pressure (20 mm), the mixture (1.37 g) was analyzed by vpc (col 3, 140°, 40 ml/min). The products were found to be composed of 2 components in the ratio 78:22 (in the order of increasing retention times) in a yield of 56%.

The 78% component was identified as exo-6-t-butoxy-endo-7-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (trans-adduct) on the basis of its spectral data: ir (neat), 3088 and 3032 cm^{-1} (w, cyclopropyl C-H stretching), 1190 (s), 1116 (s), 1064 (s), 1030 (s), all attributable to C-O stretching 806 (s) and 755 (m), both assignable C-Cl stretching; nmr (100 MHz, CCl$_4$), τ 6.22 (poorly resolved doublet of doublet, J = 2.9 Hz, 2 Hz, 1H, α-chloro proton), 6.61 (triplet, J = 2 Hz, 1H, α-butoxy proton), 7.63 (unresolved multiplet, 1H, bridgehead proton β to chlorine), 7.94 (singlet, 1H, the bridgehead proton β-t-butoxy), 8.5-8.9 (multiplets with a large singlet at 8.86, 11 H, the anti-C$_8$ proton, the t-butoxy protons, and the C$_4$ proton), 9.08 (a poorly resolved multiplet of a doublet of the AB pattern, J = 12 Hz, 1H, the syn-C$_8$ proton), 9.2-9.5 (multiplets, 2H, the C$_2$ proton and the syn-C$_4$ proton), and 9.65-9.92 (a four-peak signal with a spacing of 7 Hz between each consecutive pair of peaks, 1H, the anti-C$_3$ proton).

Anal. Calcd. for C$_{12}$H$_{19}$OCl: C, 67.13; H, 8.92. Found: C, 67.29; H, 9.07.

The 22% component was identified as exo-6-t-butoxy-exo-7-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (cis-adduct) on the basis of its spectral data: ir (neat), 3092 (w) and 3032 (s), both assignable to cyclopropyl C-H stretching, 1195 (s), 1110 (s), 1090 (s), 1080 (s), 1030 (s), all attributable to C-O stretching, 745 (s), 712 (s), both assignable to C-Cl stretching; nmr (100 MHz, CCl$_4$), τ 6.23 (doublet

of a doublet, J = 6.0 Hz, J = 2.3 Hz, 1H, α-chloro proton), 6.51

(doublet of a doublet, J = 6 Hz, 1.9 Hz, 1H, the α-t-butoxy proton),

7.69 (singlet, 1H, the bridgehead proton β to chlorine), 7.96 (singlet,

1H, the bridgehead proton β to t-butoxy), 8.55 (a doublet of the AB

pattern, J = 11 Hz, 1H, the anti-C_8 proton), 8.83 (a large singlet,

9H, the t-butoxy proton), 9.25 (an unresolved multiplet of a doublet

of the AB pattern, J = 11 Hz, 1H, the syn-C_8 proton), 9.3-9.5

(multiplet, 3H, the C_2 and C_4 protons and the syn-C_3 proton), and

9.7-9.9 (multiplet, 1H, the anti-C_3 proton).

Anal. Calcd. for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C,

67.05; H, 8.72.

Reduction of the trans-Adduct, exo-6-t-Butoxy-endo-7-chloro-

exo-tricyclo[3.2.1.0^{2,4}]octane with TBTH. A sample of the trans-

adduct (ca. 110 μl, 0.12 g, 0.56 mmol) was combined with TBTH (ca.

150 μl, 0.17 g, 0.58 mmol) and a crystal of AIBN in a small tube

and the tube sealed and placed in a 95° bath. After 12 hr the tube

was cooled and opened and the contents analyzed by vpc (col 5, 155°,

40 ml/min). There was only one product, estimated to be formed in

a yield of ca. 90%. The product was identified as exo-6-t-butoxy-exo-

tricyclo[3.2.1.0^{2,4}]octane on the basis of its spectral data and on the

basis of the similarity of its nmr spectrum to that of exo-6-hydroxy-

exo-tricyclo[3.2.1.0^{2,4}]octane: ir (neat), 3092 (w), 3016 (m), both

assignable to cyclopropyl C-H stretching, 1195 (s), 1185 (s), 1155 (s),

1088 (s), 1060 (s), 1025 (s), all attributable to C-O stretching; nmr

(100 MHz, CCl_4); τ 6.54 (doublet of a doublet of a doublet, J = 7.0 Hz,

3 Hz, 1 Hz, 1H, the α-t-butoxy proton), 7.87 (poorly resolved multi-

plet, 1H, the bridgehead proton β to t-butoxy), 7.95 (singlet, 1H, the

other bridgehead proton), 8.35 (a doublet of a doublet of a doublet of

the AB pattern, J = 12.5 Hz, 7.0 Hz, 2.2 Hz, 1 H, the endo-C_7 pro-

ton), 8.75 (triplet of a doublet, of the AB pattern, J = 12.5 Hz, 1H,

the exo-C_7 proton), 8.86 (singlet, 9 H, the t-butoxy protons), 8.96

(a poorly resolved doublet of a doublet of the AB pattern, J = 12 Hz,

1 H, the anti-C_8 proton), 9.28 (a poorly resolved multiplet of a doublet

of the AB pattern, J = 12 Hz, 1H, the syn-C_8 proton), 9.35-9.6 (multi-

plet, 3H, the C_2 and C_4 protons and the syn-C_3 proton) and 9.85-10.09

(multiplet, 1H, the anti-C_3 proton).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.91; H, 11.19. Found: C,

79.93; H, 11.15.

Reduction of the cis-adduct, exo-6-t-Butoxy-exo-7-chloro-exo-

tricyclo[3.2.1.0^{2,4}]octane with TBTH. The cis-adduct (0.044 g,

0.21 mmol) was reduced with TBTH (0.0575 g, 0.198 mmol) with

AIBN initiation under conditions identical to those employed for the

trans-adduct. Vpc analysis (col 5, 155°, 40 ml/min) showed only

one product, in a yield of ca. 64%, which had retention time and ir

spectrum identical to those of the product obtained from the trans-

adduct.

Reaction of endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene with t-Butyl-

hypochlorite. The endo-olefin (3.13 g, 29.5 mmol) in 6 ml of carbon

tetrachloride was irradiated with t-butylhypochlorite (1.57 g, 14.5

mmol) for 20 min at 40+2° with a 300 watt Sylvania light bulb as in

the case of the exo- olefin. After partial removal of solvent at

reduced pressure, the mixture was analyzed by vpc (col 3, 140°,

40 ml/min). Two adducts were observed in the ratio 43:57 in the

order of increasing retention times, formed in a yield of 59%. There

was no peak in the monochloro region.

The 43% component was identified as exo-6-t-butoxy-endo-7-

chloro-endo-tricyclo[3.2.1.0^{2,4}]octane (trans-adduct) on the basis of

its spectral data: ir (neat), 3096 (w), 3040 (w), both assignable to

cyclopropyl C-H stretching, 1190 (s), 1125 (s), 1096 (s), 1065 (s),

1040 (s), all assignable to C-Cl stretching; nmr (100 MHz, CCl$_4$),

τ 6.24 (doublet of a triplet, J = 3.4 Hz, 0.7 Hz, 1H, the α-chloro

proton), 6.58 (broad singlet, may be a poorly resolved doublet,

$W_{\frac{1}{2}}$ = 5 Hz, 1H, the α-t-butoxy proton), 7.5 (envelope, 1H, the bridge-

head proton β to chlorine), 7.9 (envelope, 1H, the bridgehead proton

β to t-butoxy), 8.0 (a broad singlet, 2H, the C$_8$ protons), 8.28 (a

pair of overlapping triplets of a doublet, J = 7 Hz, 3 Hz, 1H, the

syn-C$_3$ proton), 8.55-8.75 (multiplet, 2H, the C$_2$ and C$_4$ protons),

8.82 (singlet, 9H, the t-butoxy protons), and 9.15 (multiplet, 1H,

the anti-C$_3$ proton).

Anal. Calcd. for C$_{12}$H$_{19}$OCl: C, 67.13; H, 8.92. Found:

C, 67.10; H, 8.89.

The 57% component was identified as exo-6-t-butoxy-exo-7-

chloro-endo-tricyclo[3.2.1.0^{2,4}]octane on a consideration of its

spectral data: ir (neat), 3080 (shoulder), 3032 (shoulder), (both

assignable to cyclopropyl C-H stretching), 1190 (s), 1114 (s), 1104

(s), 1042 (s), 1000 (m), all assignable to C-O stretching, 780 (s),

770 (s), 757 (m), 750 (s), 718 (s), all assignable to C-Cl stretching;

nmr (100 MHz, CCl_4), τ 6.36 (doublet of a doublet, J = 5.6 Hz, J =

1.7 Hz, 1H, α-chloro proton), 6.68 (doublet of a doublet, J = 5.6 Hz,

J = 0.8 Hz, 1H, α-t-butoxy proton), 7.68 (envelope, 1H, the bridge-

head proton β to chlorine) 7.73 (a component of an AB pattern, J = 9.5

Hz, 1H, the anti-C_8 proton), 7.92 (envelope, 1H, the bridgehead proton

β to t-butoxy), 8.15 (multiplet of the B doublet of the AB pattern,

J = 9.5 Hz, 1H, the syn-C_8 proton), 8.60-8.80 (multiplet, 2H, the

C_2 and C_4 protons), 8.82 (singlet, 9 H, the t-butoxy protons), and

9.0-9.35 (complex multiplet, 2H, the C_3 protons).

Anal. Calcd. for $C_{12}H_{19}OCl$: C, 67.13; H, 8.92. Found: C,

67.11; H, 8.90.

Reduction of the trans-Adduct, exo-6-t-Butoxy-endo-7-chloro-

endo-tricyclo[3.2.1.0^{2,4}]octane with TBTH. The trans-adduct (ca.

65 μl, 0.081 g, 0.38 mmol) was treated with TBTH (0.114 g, 0.392

mmol) and cyclohexane (60 μl) in a small tube. Approximately 5 μl

was removed for later analysis. A crystal of AIBN was added and

the tube sealed and placed in a 95° bath for 12 hr. Vpc analysis

(col 5, 155°, 40 ml/min) showed only one product, formed in a

yield of 75% (versus cyclohexane internal standard). The product

was identified as exo-6-t-butoxy-endo-tricyclo[3.2.1.0^{2,4}]octane

on the basis of its spectral data and on the basis of the similarity of

its nmr spectrum to that of exo-6-hydroxy-endo-tricyclo[3.2.1.0^{2,4}]-

octane; ir (neat), 3064 (w), 3016 (shoulder), both assignable to cyclo-

propyl C-H stretching, 1194 (s), 1086 (s) and 1030 (s), all assignable

to C-O stretching; nmr (100 MHz, CCl$_4$), τ 6.74 (doublet of doublets,

J = 6.4 Hz, 3.0 Hz, finer splitting of each of the lines to about 0.5

Hz was also observable, 1H, α-t-butoxy proton), 7.8 (unresolved

multiplet, 1H, bridgehead proton β to t-butoxy), 8.0 (unresolved

multiplet, 1H, the other bridgehead proton), 8.2 (broad singlet, 2H,

the C$_8$ protons), 8.6-8.85 (complex multiplets, 4H, protons on C$_7$,

C$_2$ and C$_4$), 8.9 (singlet, 9H, t-butoxy protons), 9.1-9.45 (complex

multiplets, 2H, protons on C$_3$).

Anal. Calcd. for C$_{12}$H$_{20}$O: C, 79.91; H, 11.19. Found: C,

79.80; H, 11.00.

Reduction of the cis-Adduct, exo-6-t-Butoxy-exo-7-chloro-

endo-tricyclo[3.2.1.0^{2,4}]octane with TBTH. A sample of the cis-

adduct (ca. 130 µl, 0.152 g, 0.709 mmol) was reduced with TBTH

(ca. 185 µl, 0.212 g, 0.729 mmol), cyclohexane (130 µl) and a crystal

of AIBN under conditions identical to those used for the trans-isomer.

Vpc analysis (col 5, 155°, 40 ml/min) showed only one product in a

yield of ca. 97% (versus cyclohexane internal standard). The sole

product was identical to the one obtained from the trans-adduct as

observed by comparison of vpc retention times and ir spectra.

Reaction of Deltacyclene with t-Butylhypochlorite. The reaction

of deltacyclene, synthesized by the method of Katz et al. (103, 104)

(4.00 g, 34 mmol) in carbon tetrachloride (11 ml) with t-butylhypo-

chlorite (1.84 g, 17 mmol) was performed exactly as above for the

other olefins. Vpc analysis of the products (col 3, 155°, 45 ml/min)

after partial removal of solvent at reduced pressure (20 mm), showed

4 peaks in the ratio 12.5:4.5:66:17 in the order of increasing retention

times. The 12.5% component showed a multiplicity of signals includ-

ing aromatic proton signals in the nmr and possibly arose from indene,

a contaminant in deltacyclene. The 4.5% component on further vpc

analysis was found to be a mixture of 4 components none of which

showed the correct molecular weight for the monochloride or the

t-butylhypochlorite addition product on mass spectral analysis.

The 66% and 17% components were identified as the trans- and

cis-adducts on the basis of their spectral data and on the basis of

their reduction to exo-8-t-butoxydeltacyclane. The trans-adduct

(66% component) had the following spectral characteristics: ir (neat),

3056 (w), assignable to cyclopropyl C-H stretching, 1185 (s), 1152

(m), 1060 (s), 1021 (s), all assignable to C-O stretching, 800 (s),

790 (s), 775 (m), 733 (m), all assignable to C-Cl stretching; nmr

(100 MHz, CCl_4): τ 6.07 (doublet of a doublet, J = 4 Hz, J = 2 Hz, 1H, α-chloroproton), 6.24 (poorly resolved doublet, J = 2 Hz, 1H, α-t-butoxy proton), 7.8 (unresolved multiplet, 1H, bridgehead proton β to chlorine), 7.88 (unresolved multiplet, 1H, bridgehead proton β to t-butoxy), 8.15 (unresolved triplet, 1H, C-6 proton), 8.42 (singlet, 2H, C-5 protons:, 8.74 (singlet, 2H, C-2 and C-3 protons), 8.82 (singlet, 9H, t-butoxy protons), 9-9.15 (a doublet of a doublet of a doublet, J = 11, 6, 2 Hz, 1H, C-4 proton).

Anal. Calcd. for $C_{13}H_{19}OCl$: C, 68.85; H, 8.45. Found: C, 68.58; H, 8.23.

The cis-adduct (17% component) was contaminated to the extent of about 32% by an unidentified material; ir (neat), 3056 (w), assignable to cyclopropyl C-H stretching, 1185 (m), 1086 (s), both assignable to C-O stretching, 800 (s), assignable to nortircyclene ring, 765 (w), 715 (w), both assignable to C-Cl stretching; nmr (100 Mz, CCl_4), τ 5.9 (doublet, J = 6.0 Hz), 6.15 (doublet, J = 6 Hz), 7.35 (poorly resolved multiplet), 7.64 (envelope), 7.88 (envelope), 8.0-8.3 (multiplets), 8.48 (a broad singlet), 8.52-8.98 (multiplets with a large singlet at 8.85), and 9.05-9.22 (multiplet). Integration data were misleading due to contamination of the sample.

Anal. Calcd. for $C_{13}H_{19}OCl$: C, 68.85; H, 8.45. Found: C, 68.50; H, 8.23.

Reduction of the <u>trans</u>-Adduct,<u>exo</u>-8-t-Butoxy-<u>endo</u>-9-chloro-

<u>deltacyclane with TBTH</u>. A sample of the <u>trans</u>-adduct (0.1780 g,

0.786 mmol) was treated with TBTH (<u>ca</u>. 210 μl, 0.247 g, 0.849

mmol) and cyclohexane (<u>ca</u>. 100 μl) in a small tube. Approximately

4 μl was removed for later analysis. A crystal of AIBN was added and

the tube sealed and placed in a 95° bath for 10 hr. After cooling to

room temperature, the tube was opened and the contents analyzed by

vpc (col 5, 155°, 40 ml/min). There was only one product (<u>ca</u>. 81%

yield versus cyclohexane internal standard) which was identified as

<u>exo</u>-8-t-butoxy deltacyclane on the basis of its spectral data and on

the basis of the similarity of its nmr spectrum to that of <u>exo</u>-8-

hydroxydeltacyclane; ir (neat), 3056 (w), assignable to cyclopropyl

C-H stretching, 1190 (s), 1178 (s), 1136 (m), 1070 (s), 1040 (s), all

assignable to C-O stretching; nmr (100 MHz, CCl_4); τ 6.2 (poorly

resolved multiplet of a doublet, J = 6.6 Hz, 1H, α-t-butoxy proton),

8-8.25 (a series of poorly resolved multiplets, 5H, bridgehead pro-

tons on C-1 and C-7, <u>exo</u>- and <u>endo</u>- protons on C-9 and the proton on

C-6), 8.46 (singlet, 2H, C-5 protons), 8.85 (large singlet with a

poorly resolved multiplet vuried under it, 10H, t-butoxy and one of

the tertiary cyclopropyl protons) and 9.25 (doublet of a triplet, J = 4

Hz, J = 1 Hz, 2H, the remaining cyclopropyl protons).

<u>Anal</u>. Calcd. for $C_{13}H_{20}O$: C, 81.17; H, 10.49. Found: C,

81.30; H, 10.62.

Reduction of the cis-Adduct, exo-8-t-Butoxy-exo-9-chloro-deltacyclane with TBTH. The cis-adduct (0.0490 g, 0.22 mmol) was reduced with TBTH (0.0680 g, 0.23 mmol), cyclohexane (ca. 40 μl) and a crystal of AIBN at 95° for 10 hr. Vpc analysis (col 5, 155°, 40 ml/min) showed 2 products in the ratio 68:32 in a yield of ca. 67% versus cyclohexane internal standard). The 68% component was identical (retention time and ir) to the sole product obtained on reduction of the trans-adduct. The 32% component could not be isolated in sufficient quantities to enable its characterization.
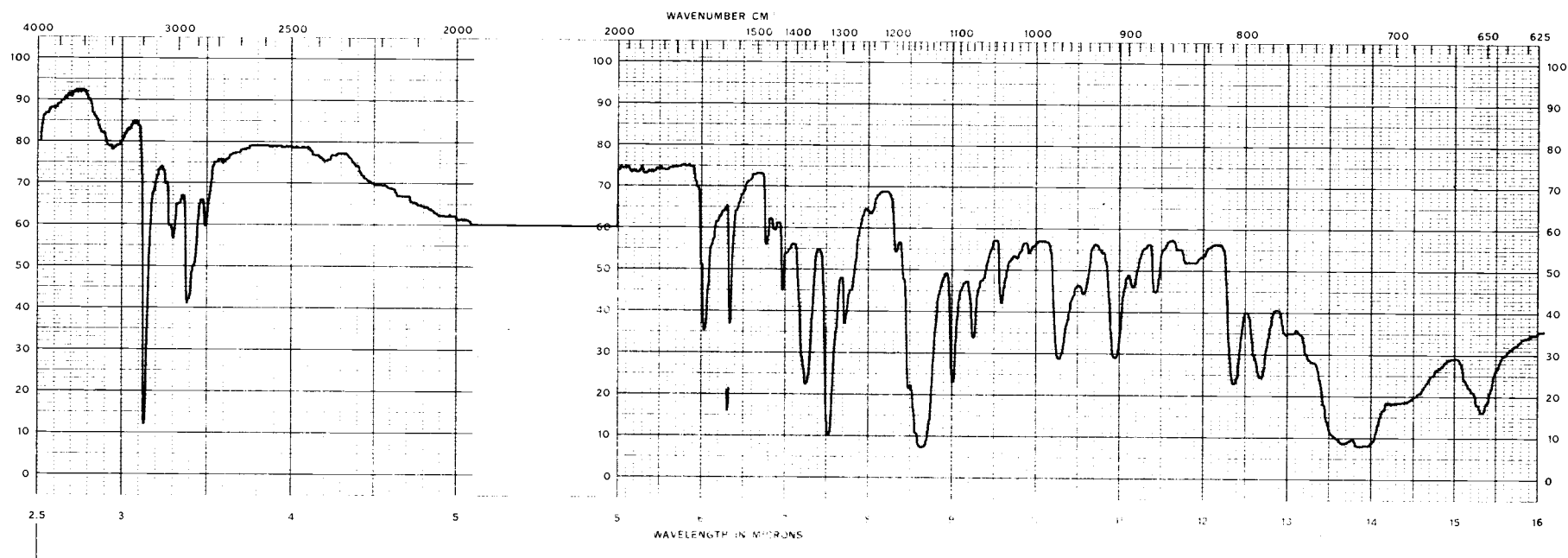
Figure 1. Infrared Spectrum of endo-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone (KBr pellet).
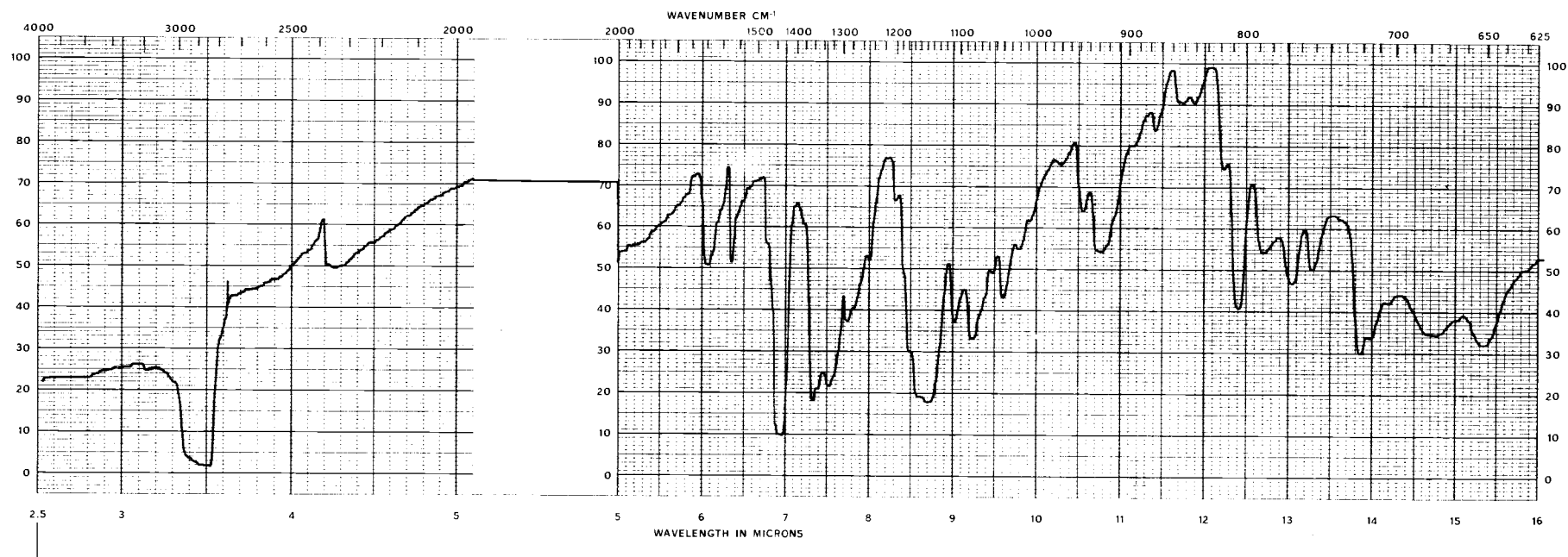
Figure 2.   Infrared Spectrum of <u>endo</u>-Tricyclo[3.2.1.0^{2,4}]octan-8-one Tosylhydrazone-N-d$_1$
(nujol mull, salt plates).
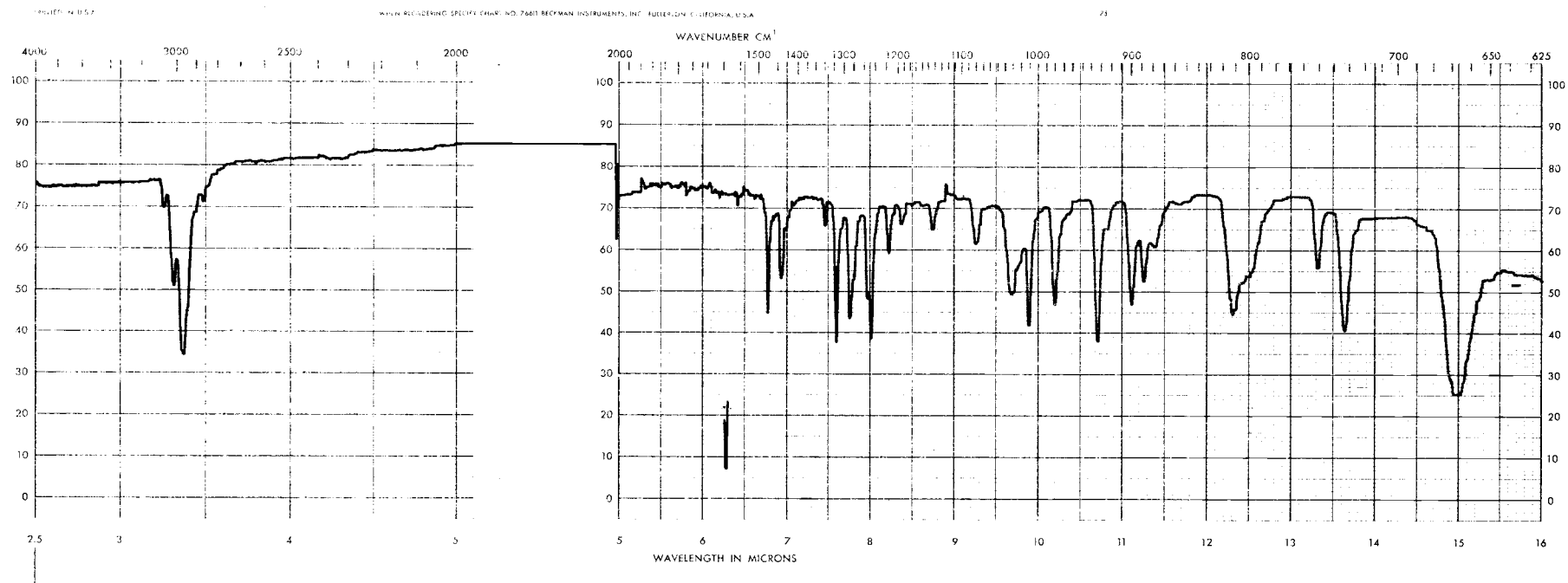
Figure 3. Infrared Spectrum of exo-6-Chloro-exo-tricyclo-[3.2.1.0^{2,4}]octane (neat, salt plates).
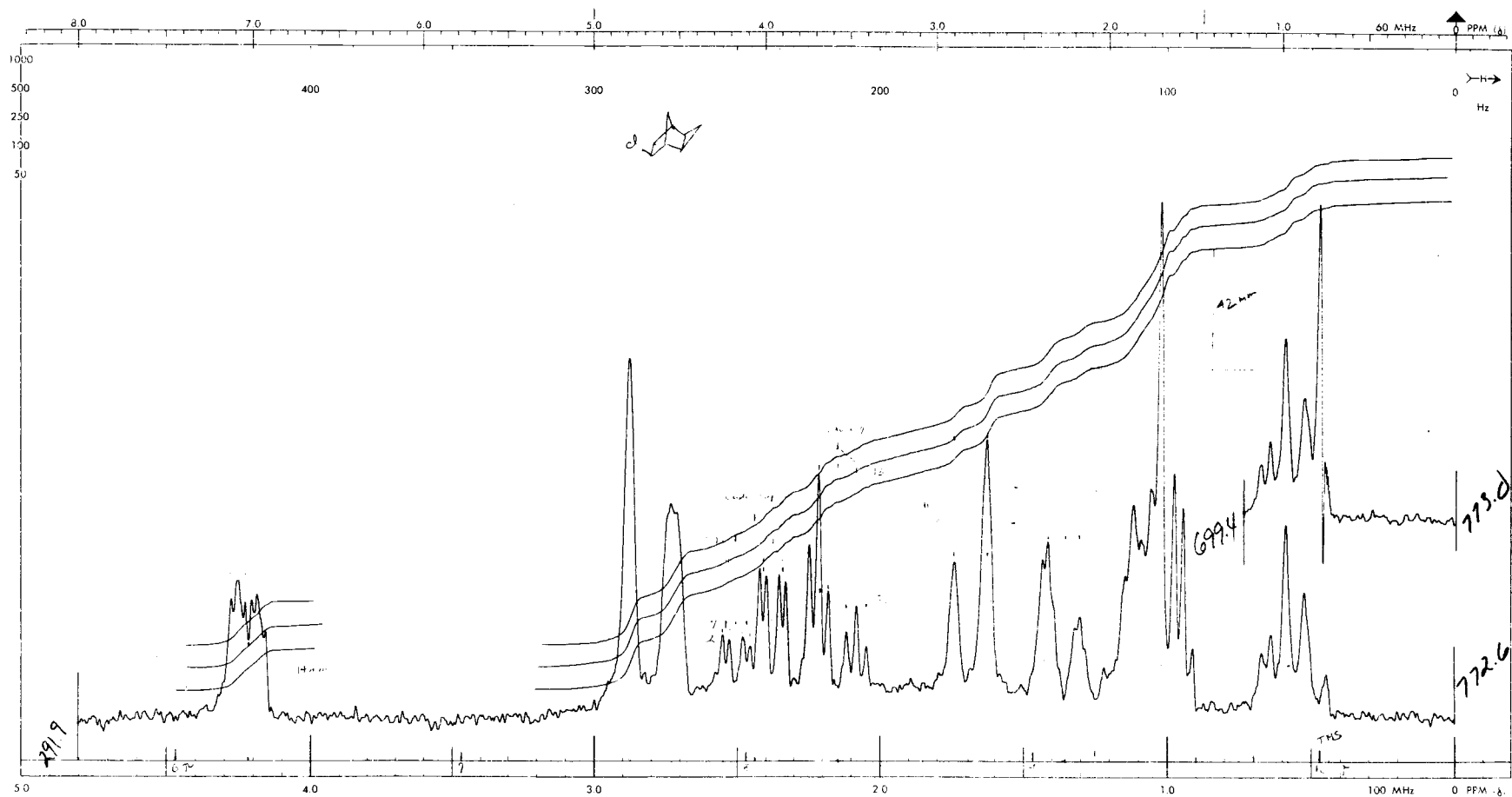
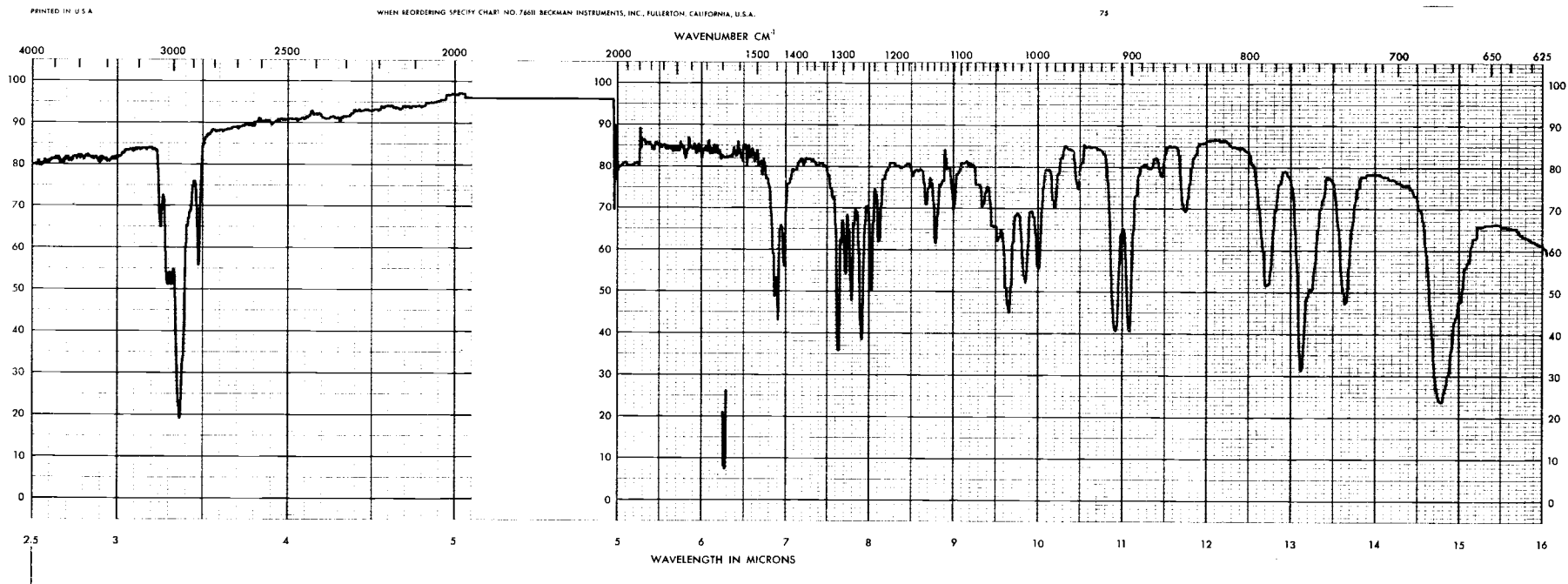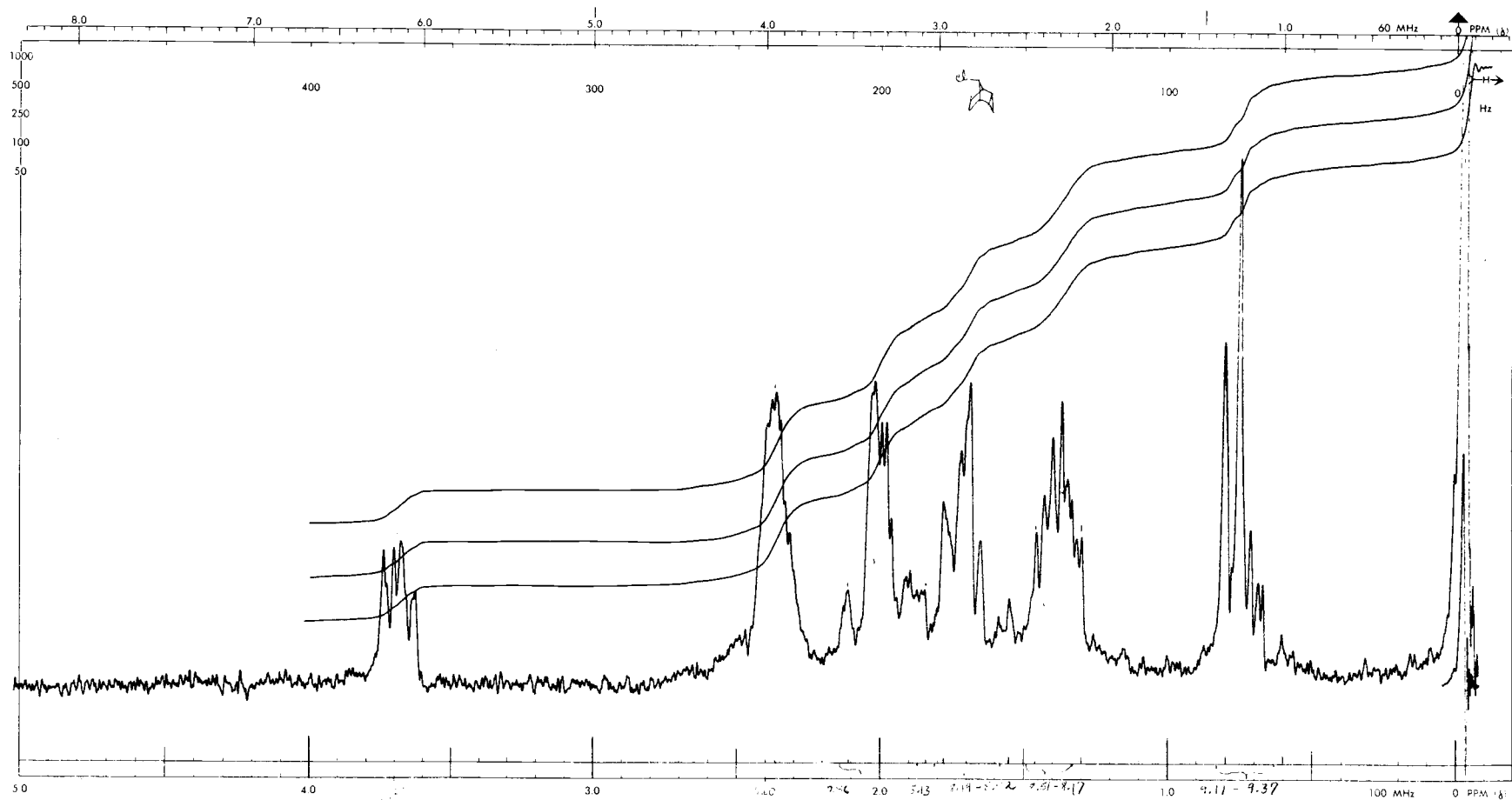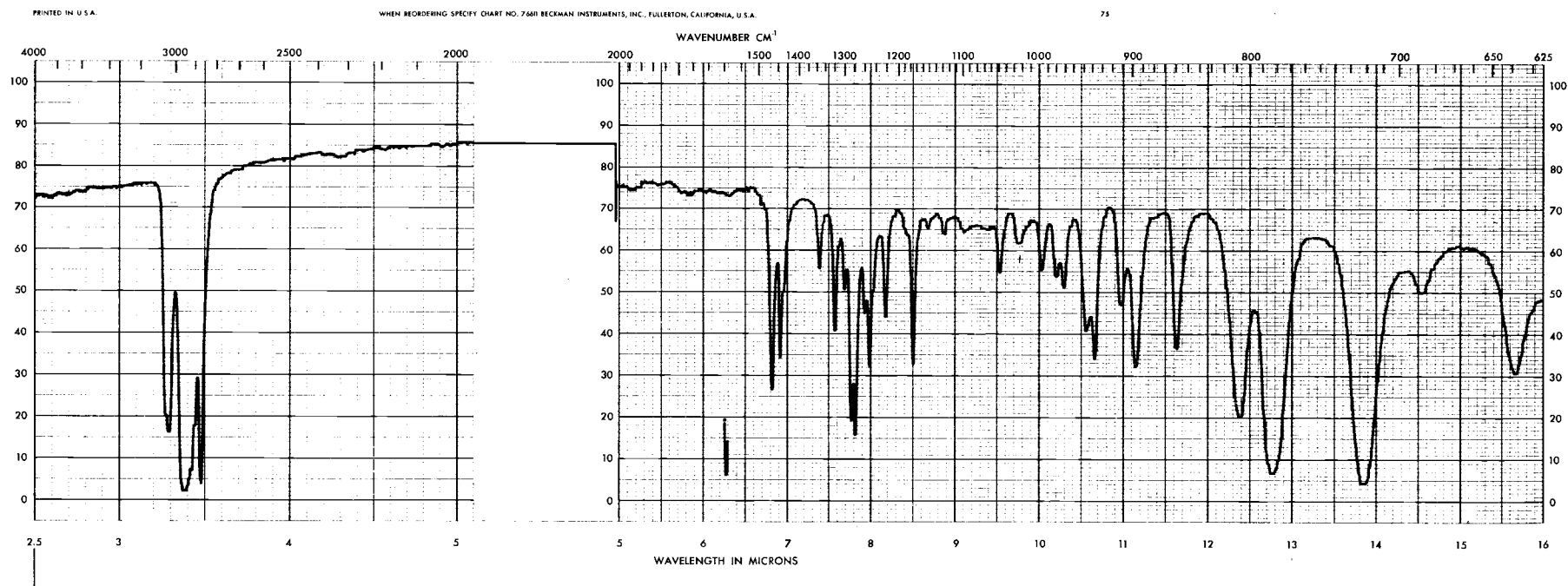Figure 4. 100 MHz nmr Spectrum (CCl$_4$) of exo-6-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane.
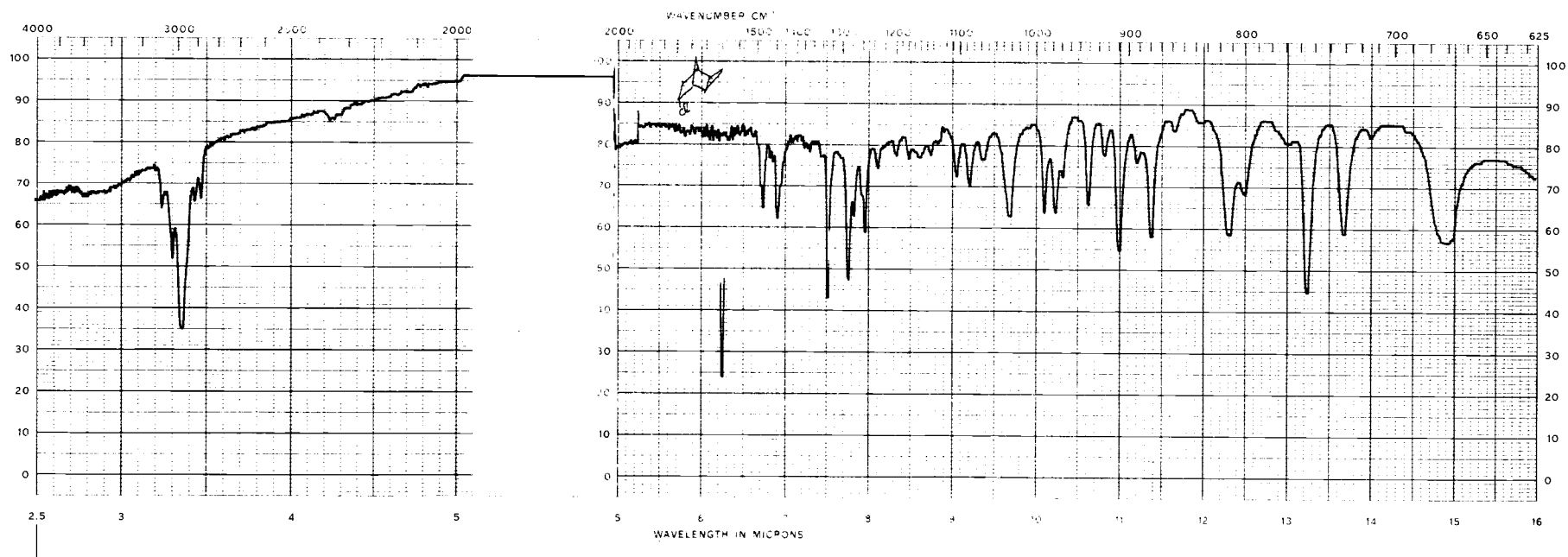
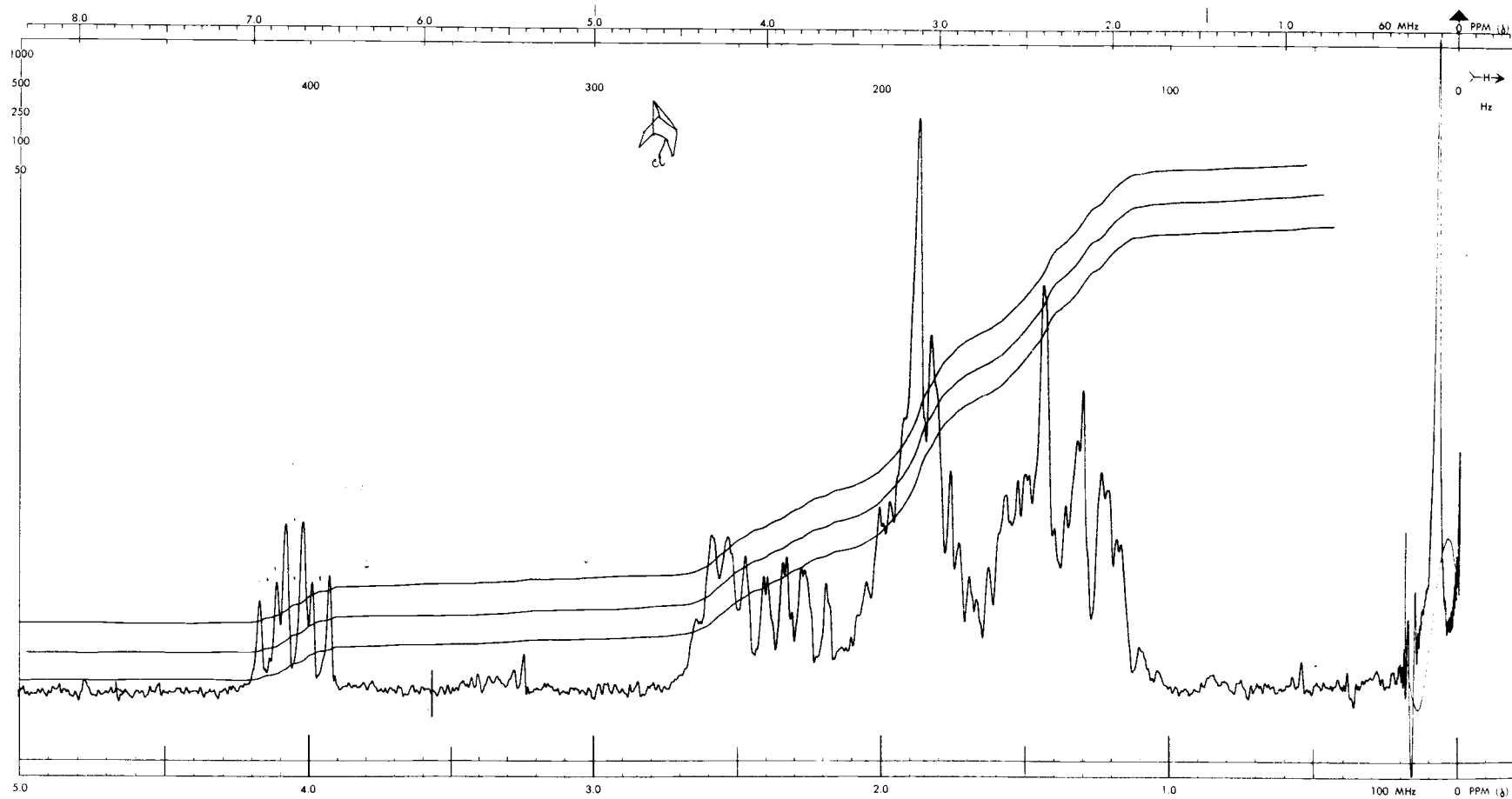Figure 5. Infrared Spectrum of endo-6-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
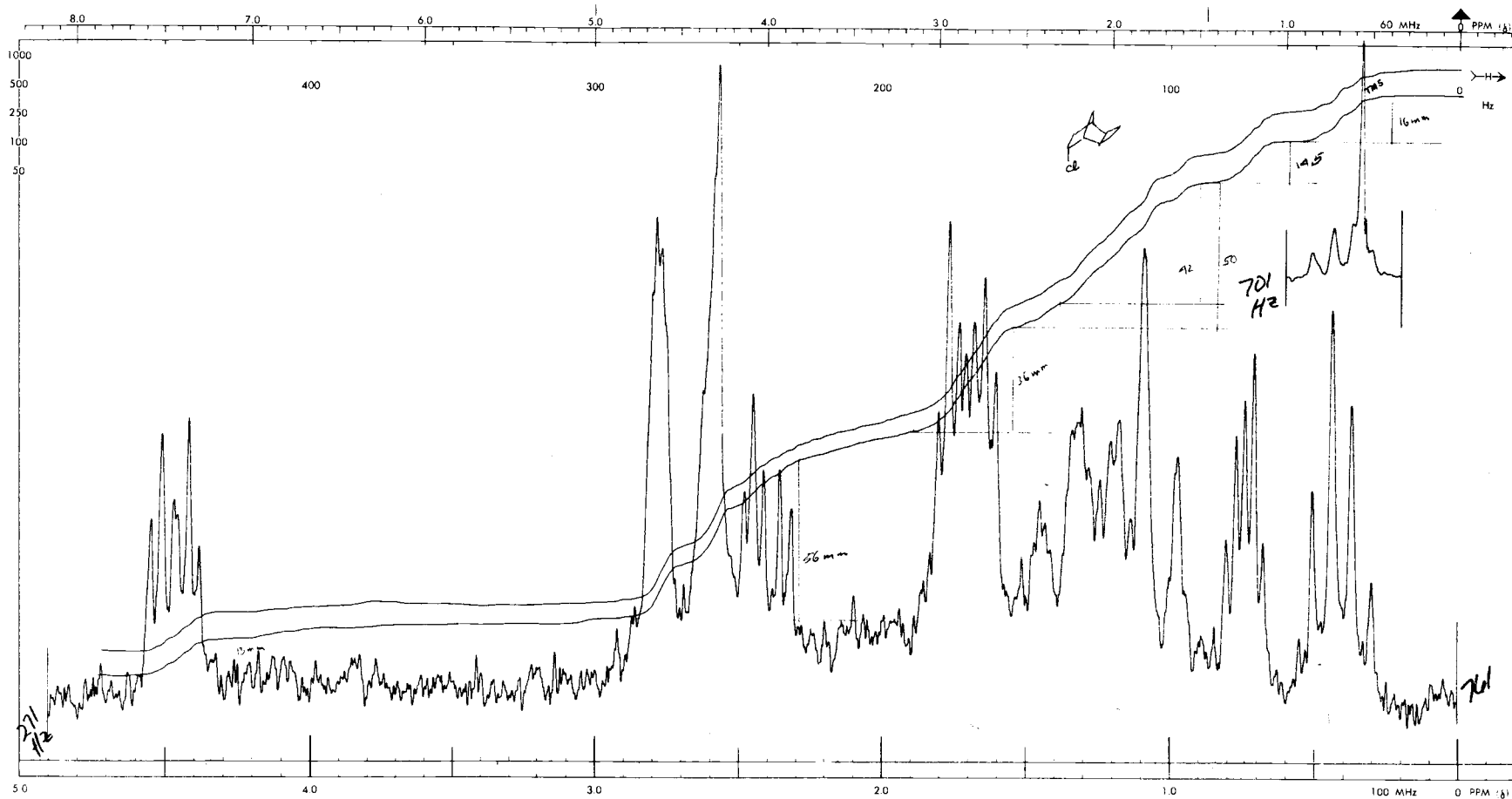
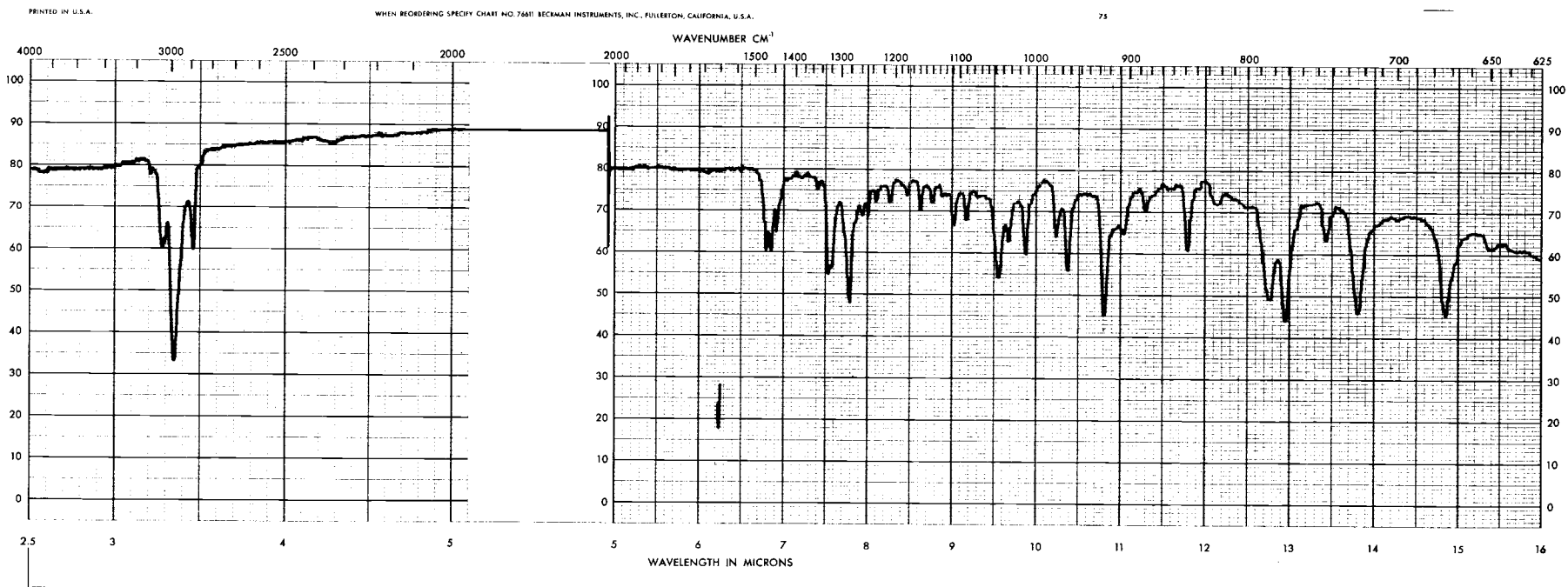Figure 6. 100 MHz nmr Spectrum (CCl_4) of endo-6-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane.
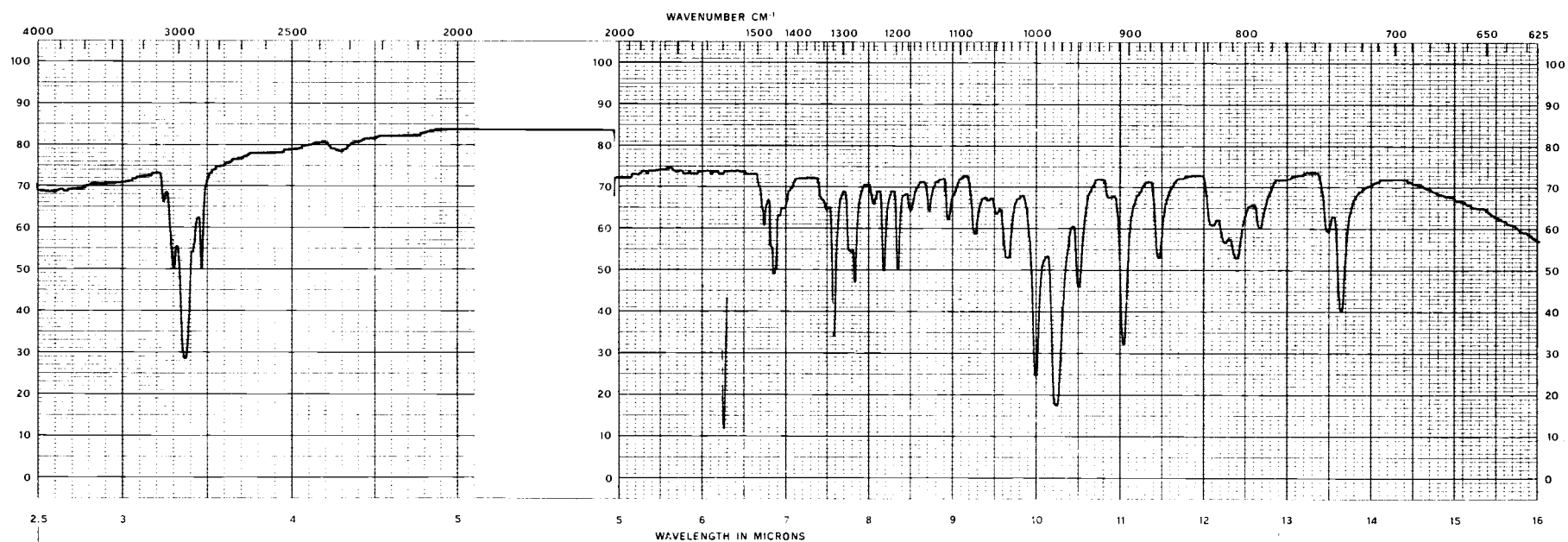
Figure 7. Infrared Spectrum of 1-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
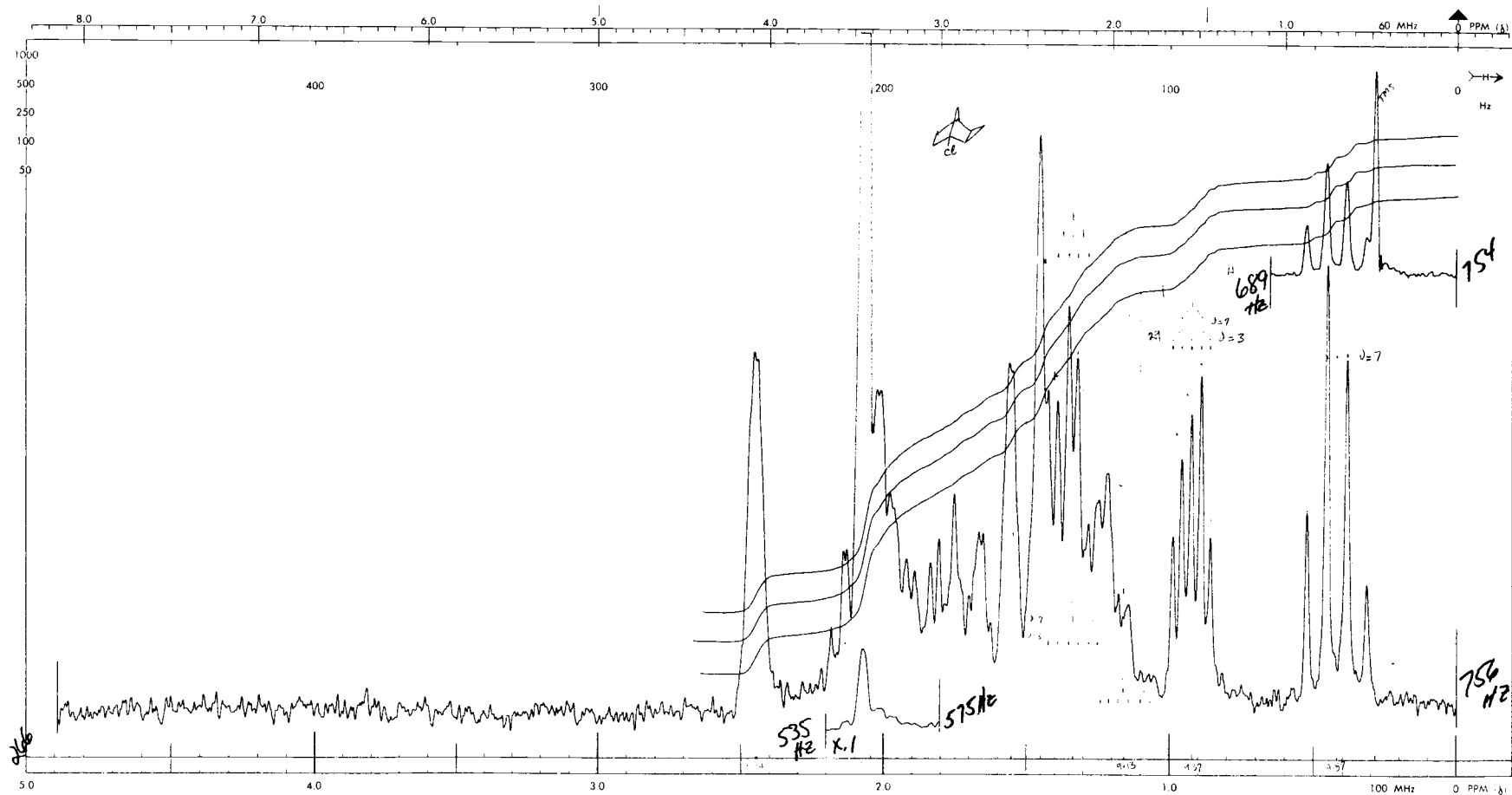
Figure 8. 100 MHz nmr Spectrum (CCl_4) of 1-Chloro-exo-tricyclo[3.2.1.0^{2,4}]octane.

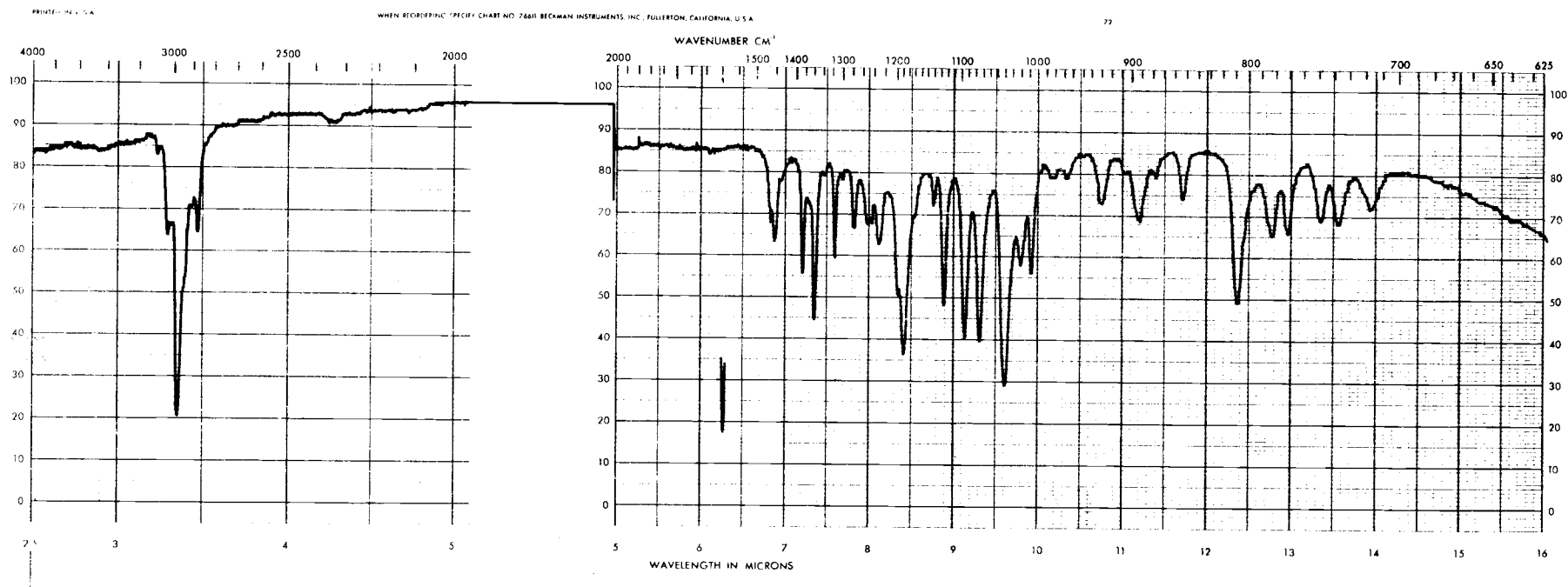Figure 9.   Infrared Spectrum of anti-8-Chloro-endo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).

Figure 10.   100 MHz nmr Spectrum (CCl$_4$) of anti-8-Chloro-endo-tricyclo[3.2.1.0^{2,4}]octane.

Figure 11. Infrared Spectrum of endo-2-Chlorotricyclo[3. 3. 0. 0$^{4, 6}$]octane (neat, salt plates).

Figure 12. 100 MHz nmr Spectrum (CCl$_4$) of <u>endo</u>-2-Chloro-tricyclo[3.3.0.0^{4,6}]octane.

Figure 13.   Infrared Spectrum of Unidentified Monochloride Product in the Photochlorination of endo-Tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
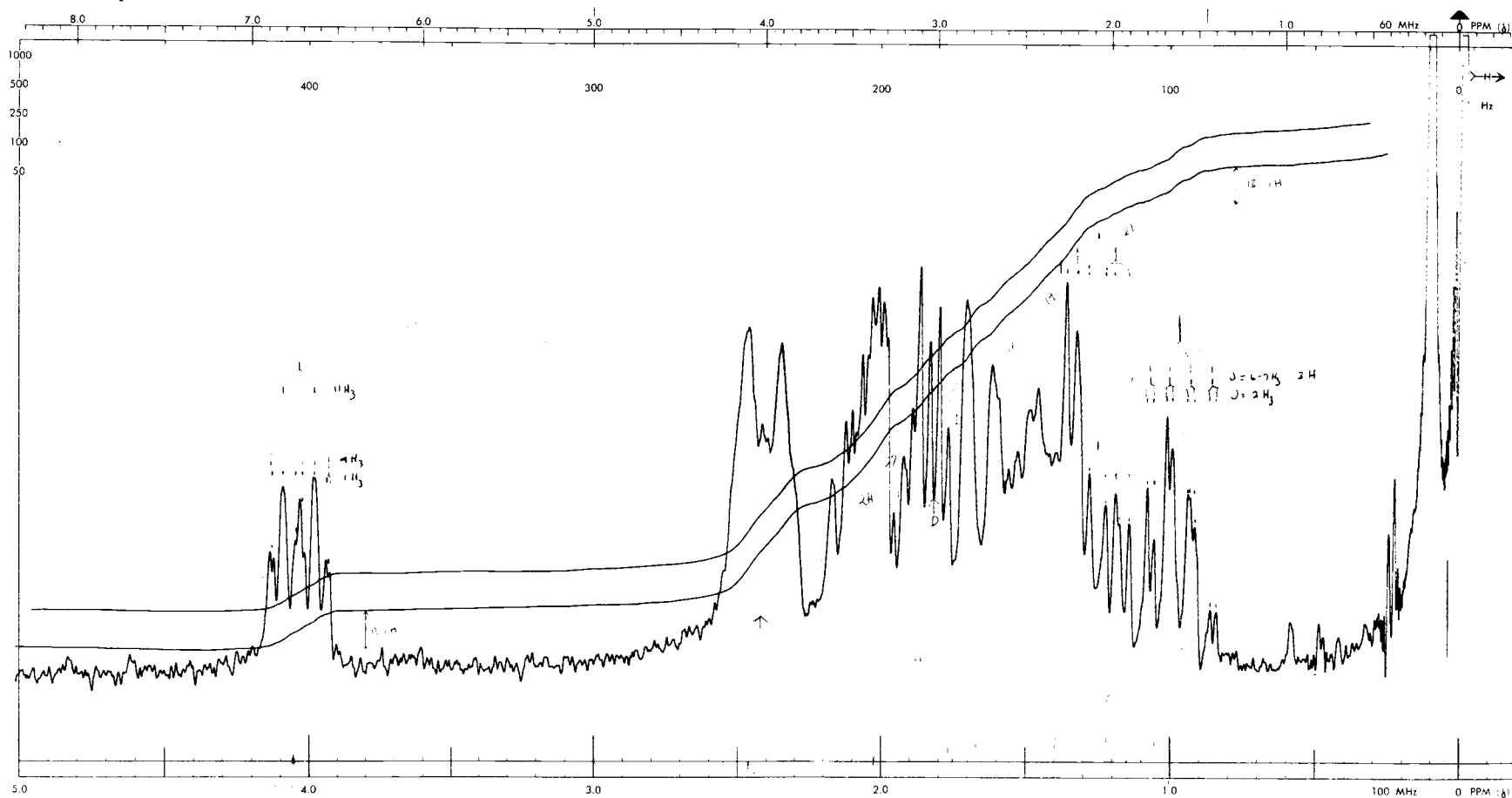
Figure 14. 100 MHz nmr Spectrum (CCl$_4$) of Unidentified Monochloride Product in the Photochlorination of <u>endo</u>-Tricyclo[3.2.1.0^{2,4}]octane.

Figure 15. Infrared Spectrum of exo-6-t-Butoxy-endo-7-chloro-endo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
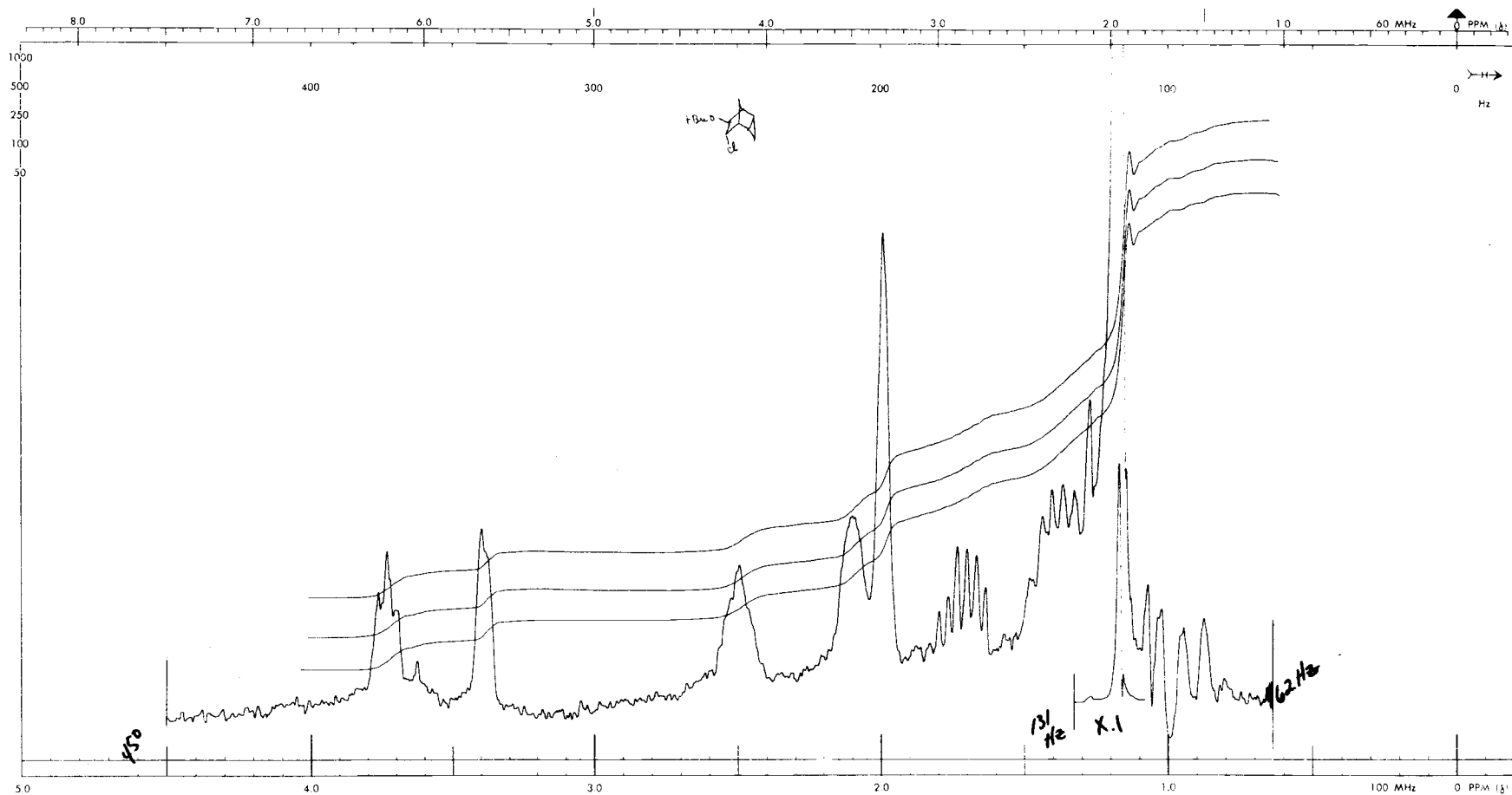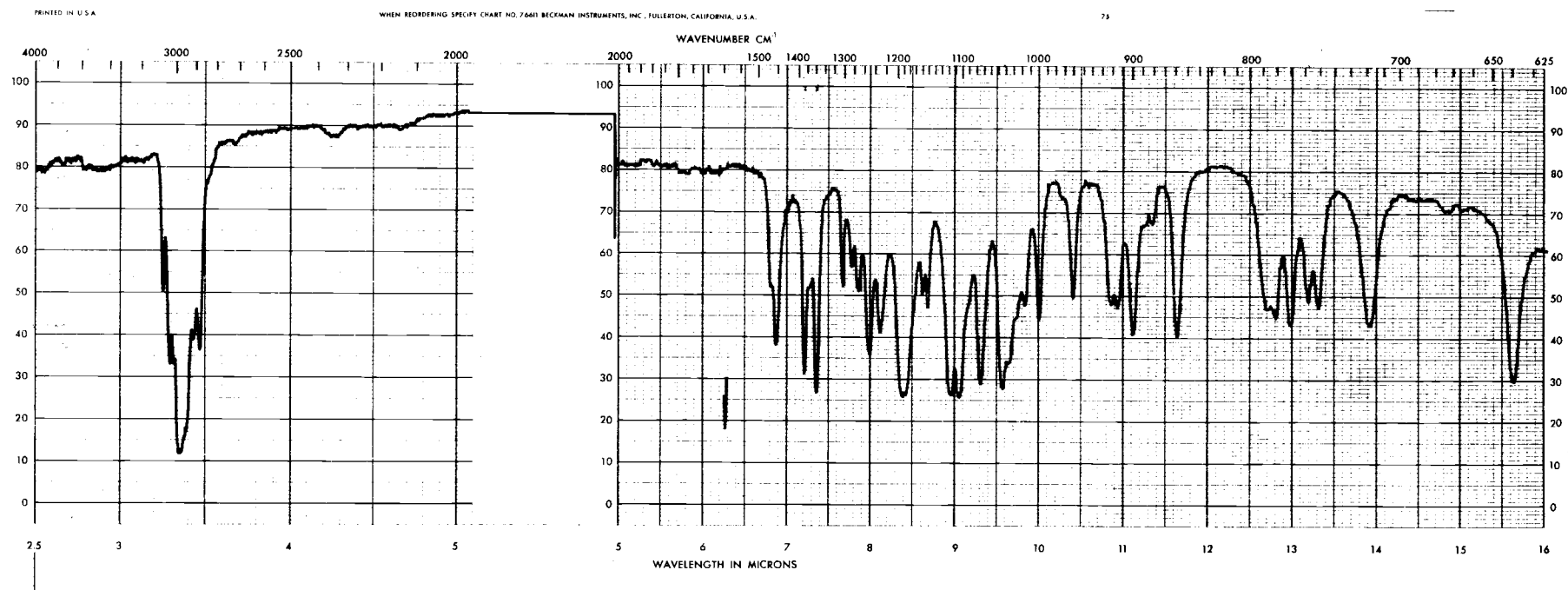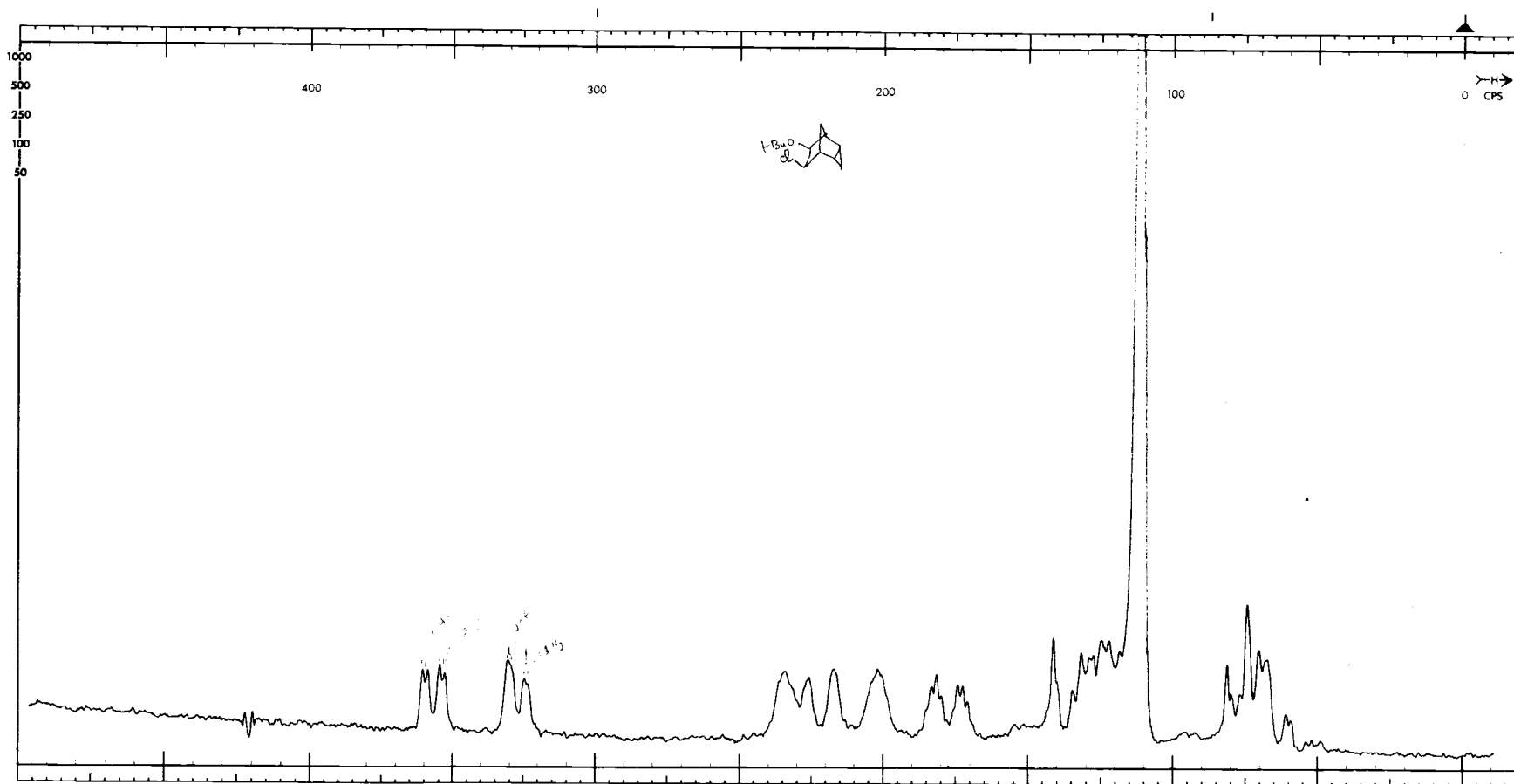
Figure 16.   100 MHz nmr Spectrum (CCl_4) of <u>exo</u>-6-t-Butoxy-<u>endo</u>-7-chloro-<u>endo</u>-tricyclo-[3.2.1.0^{2,4}]octane.

WAVENUMBER CM⁻¹

WAVELENGTH IN MICRONS

Figure 17.   Infrared Spectrum of exo-6-t-Butoxy-exo-7-chloro-endo-tricyclo[3.2.1.0^{2,4}]octane
(neat, salt plates).

Figure 18.   100 MHz nmr Spectrum (CCl_4) of <u>exo</u>-6-t-Butoxy-<u>exo</u>-7-chloro-<u>endo</u>-tricyclo-[3.2.1.0^{2,4}]octane.

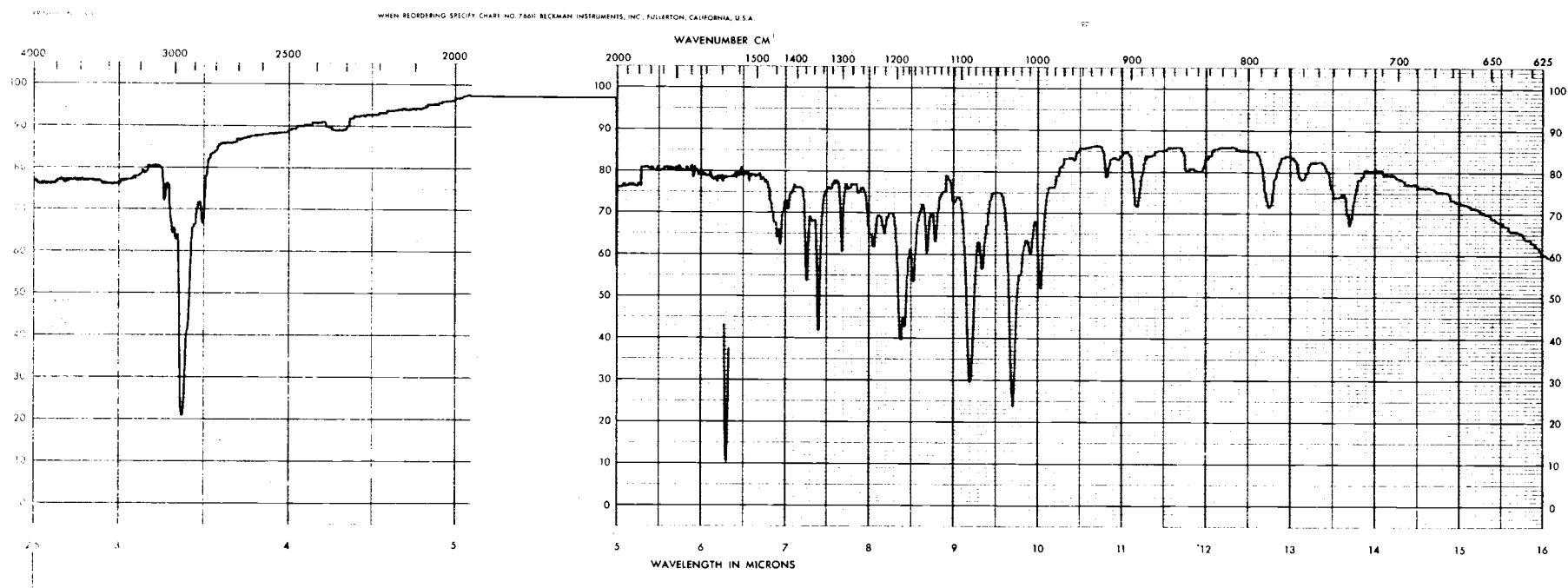**WAVENUMBER CM⁻¹**

WAVELENGTH IN MICRONS

Figure 19. Infrared Spectrum of exo-6-t-Butoxy-endo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
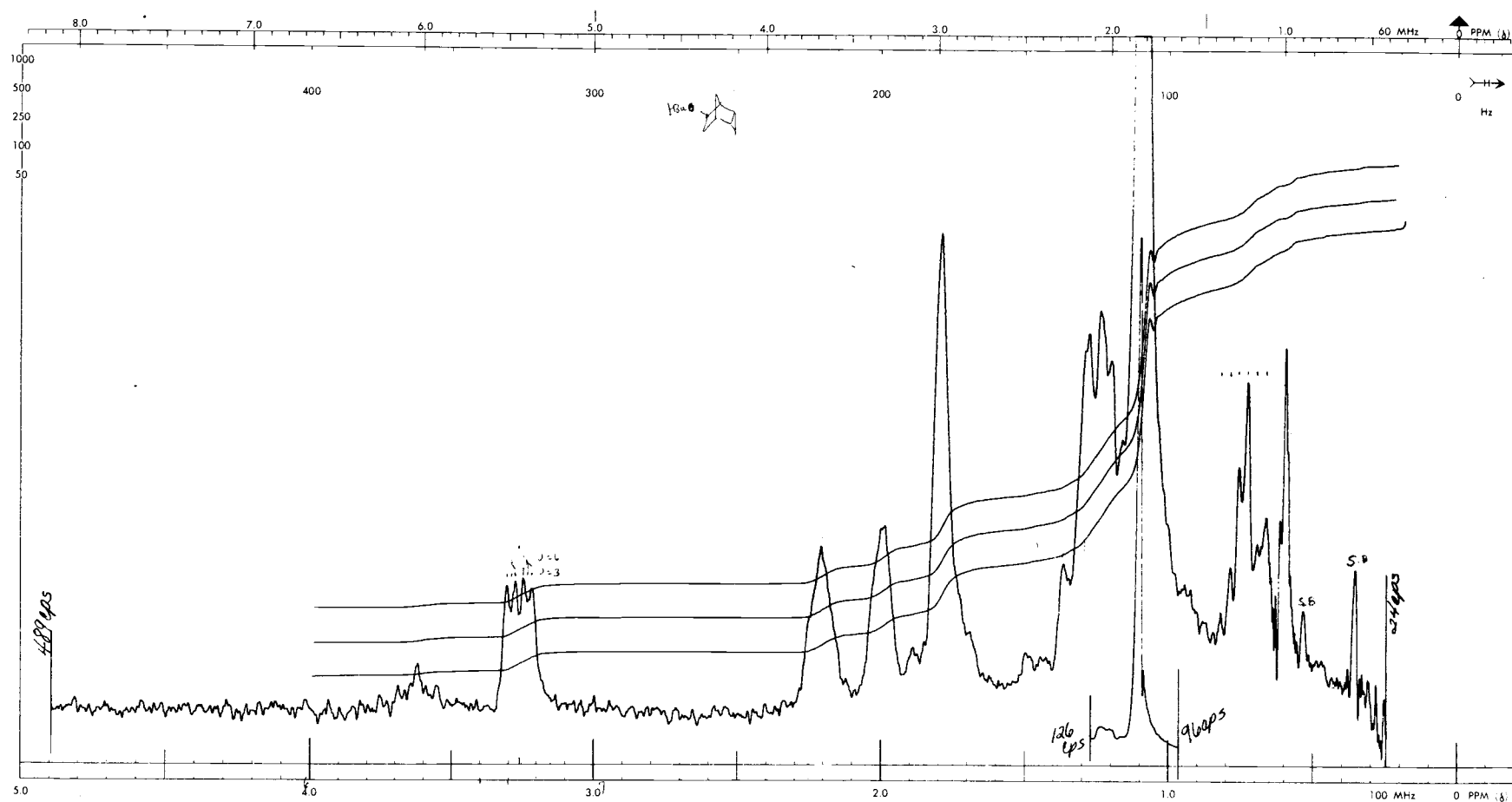
Figure 20. 100 MHz nmr Spectrum (CCl_4) of exo-6-t-Butoxy-endo-tricyclo 3.2.1.0^{2,4}]octane.

Figure 21. Infrared Spectrum of exo-6-t-Butoxy-endo-7-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).

Figure 22. 100 MHz nmr Spectrum (CCl$_4$) of exo-6-t-Butoxy-endo-7-chloro-exo-tricyclo[3.2.1.0^{2,4}]-octane.
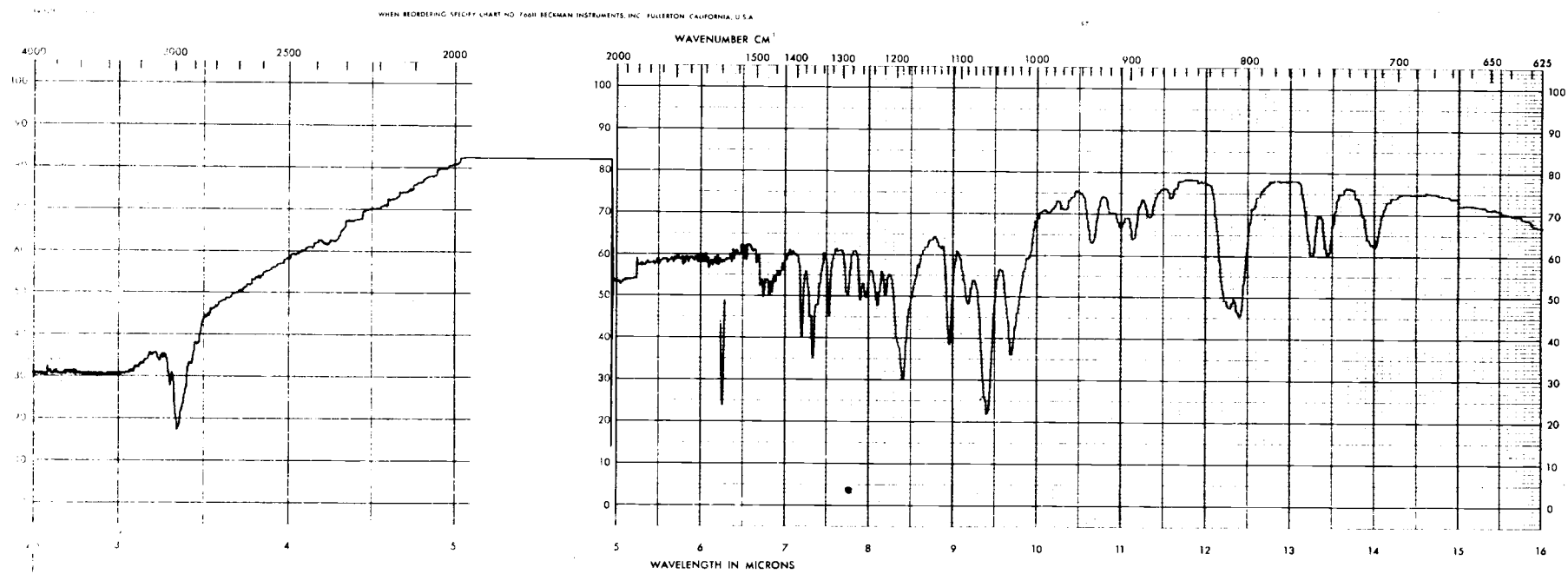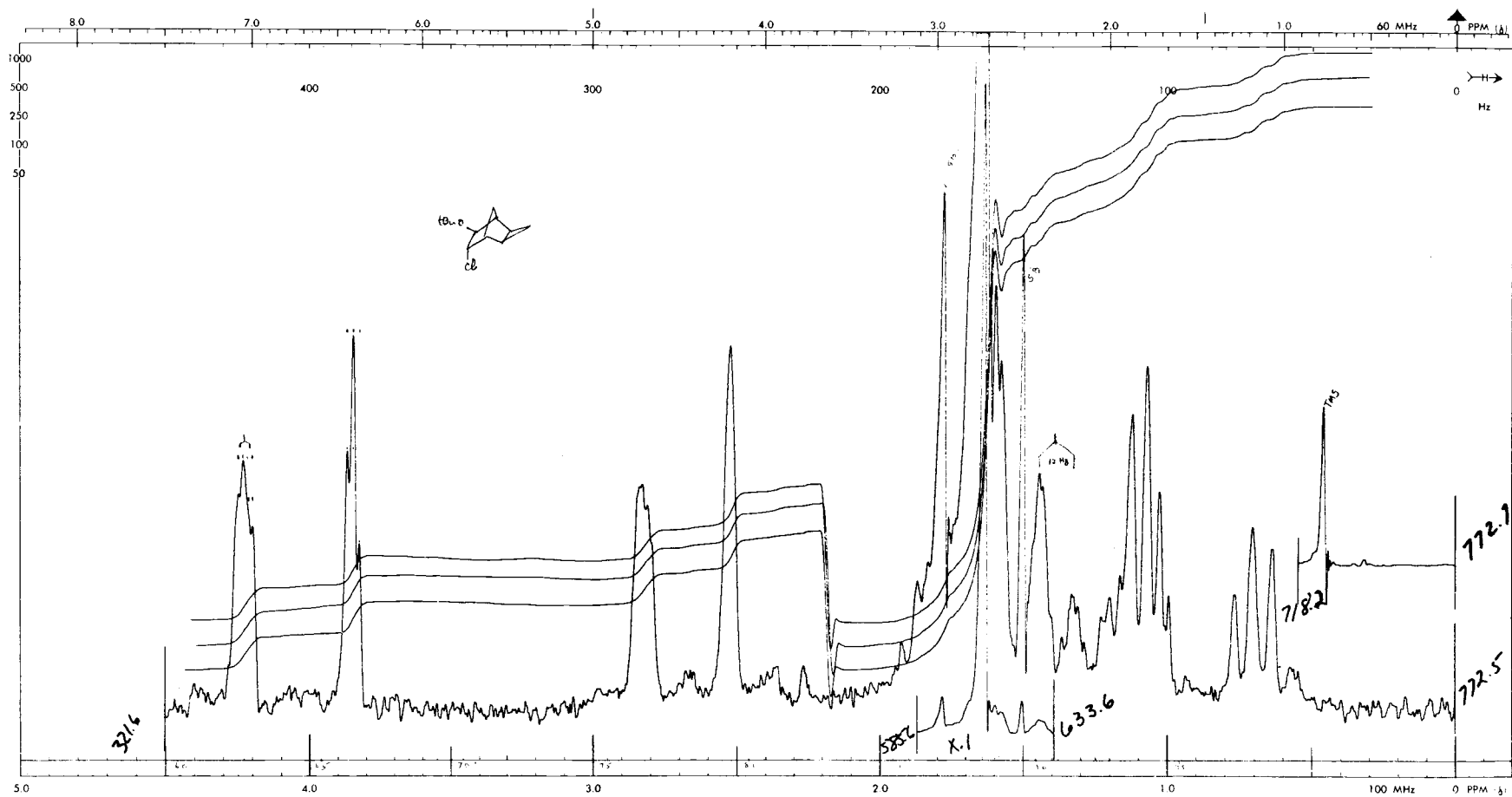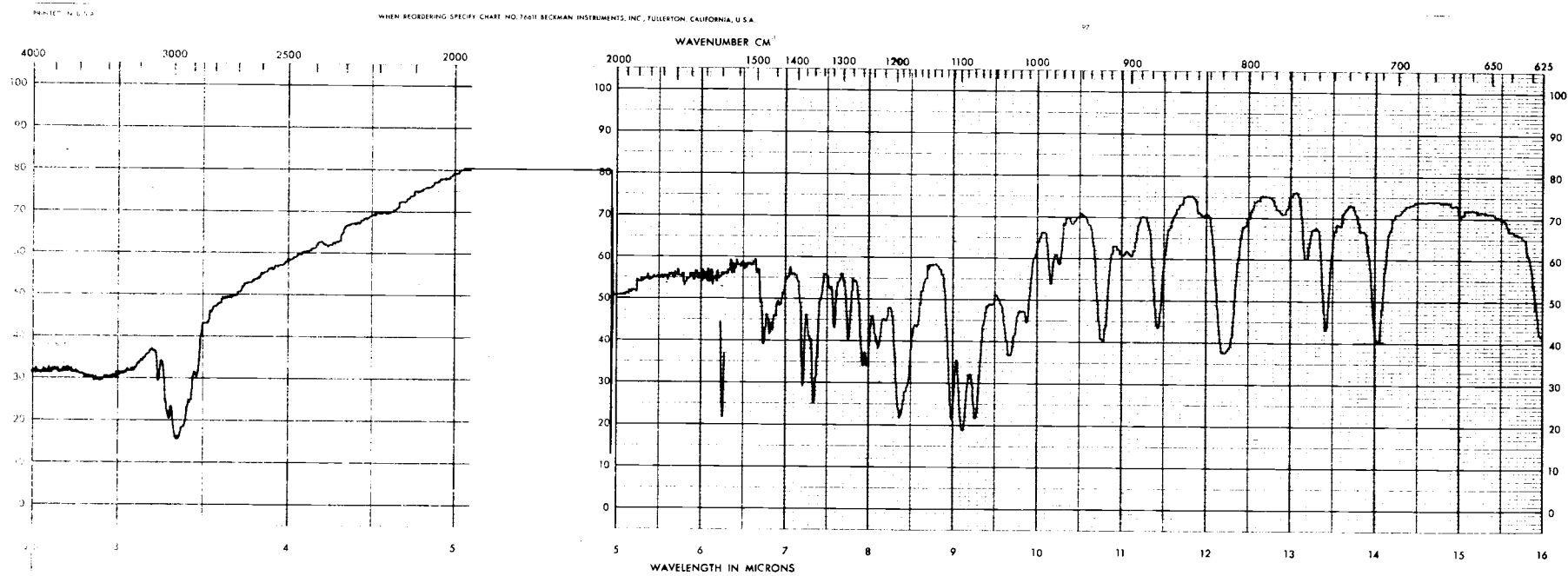
Figure 23. Infrared Spectrum of exo-6-t-Butoxy-exo-7-chloro-exo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
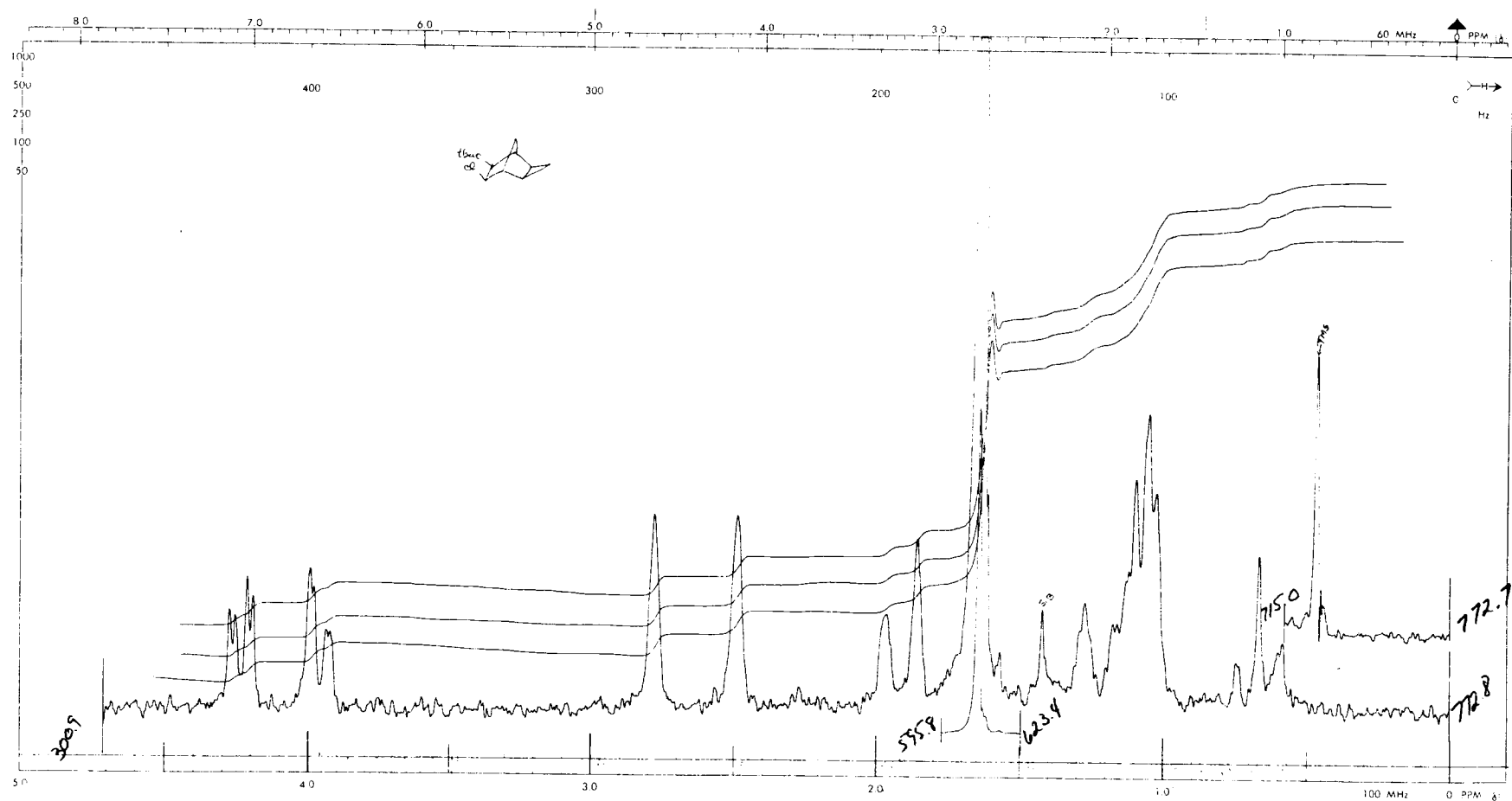
Figure 24. 100 MHz nmr Spectrum (CCl$_4$) of <u>exo</u>-6-t-Butoxy-<u>exo</u>-7-chloro-<u>exo</u>-tricyclo-[3.2.1.0^{2,4}]octane.
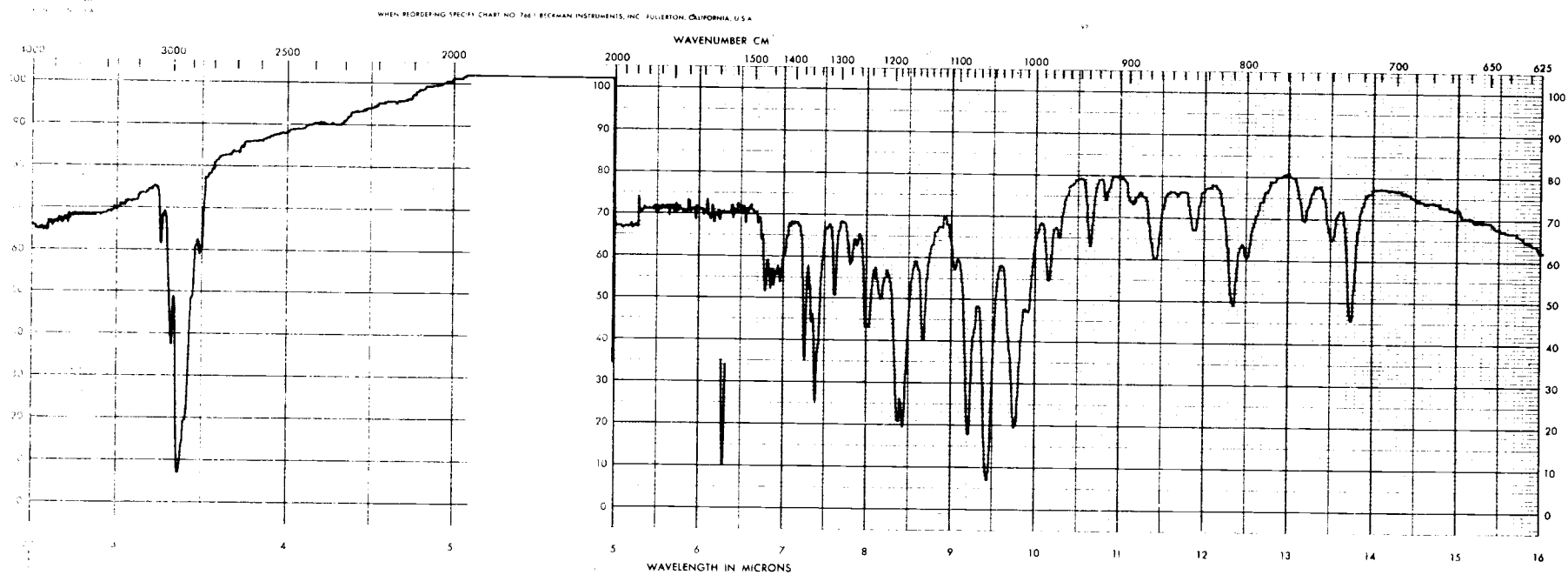
Figure 25. Infrared Spectrum of exo-6-t-Butoxy-exo-tricyclo[3.2.1.0^{2,4}]octane (neat, salt plates).
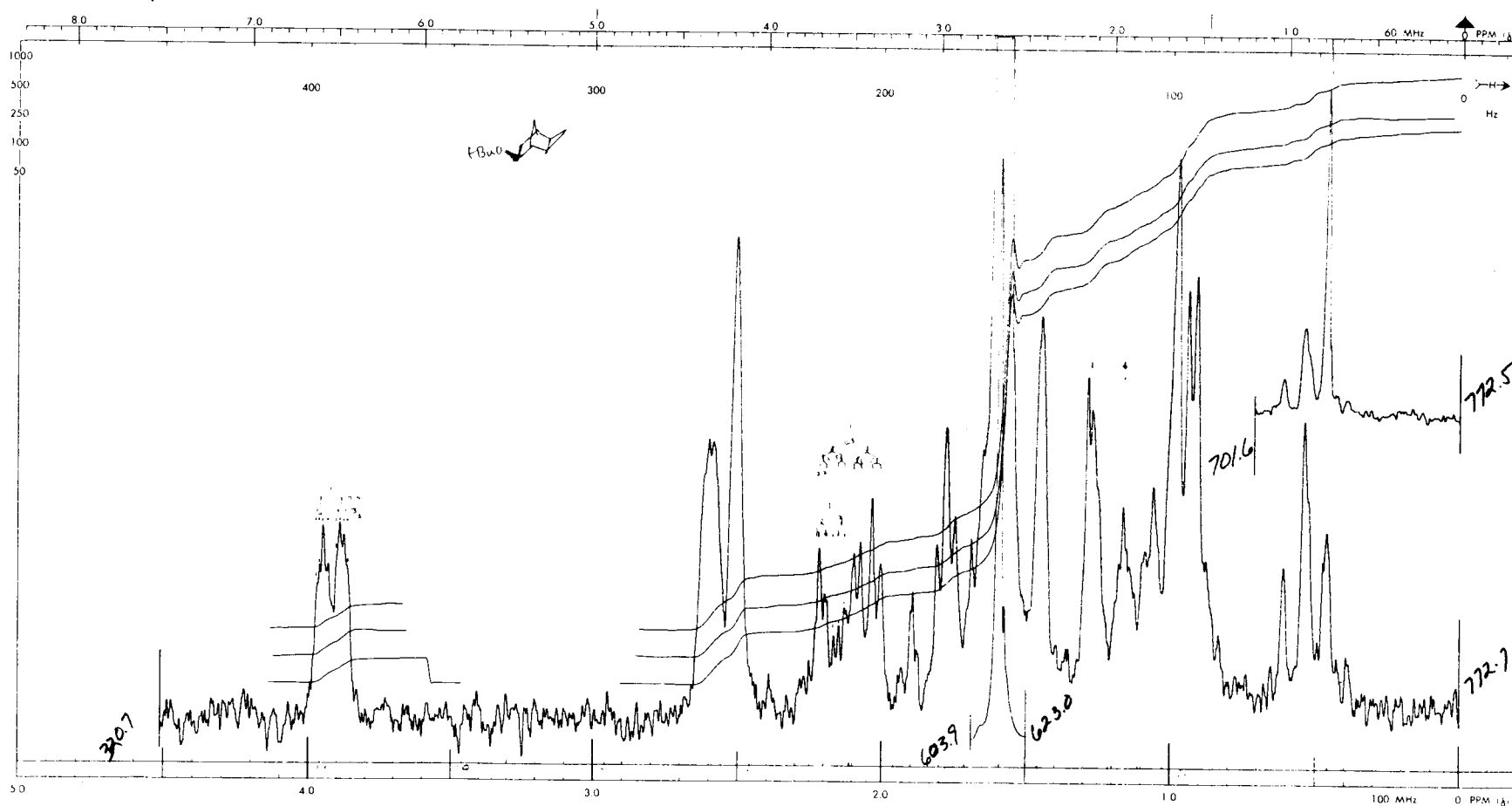
Figure 26. 100 MHz nmr Spectrum (CCl_4) of exo-6-t-Butoxy-exo-tricyclo[3.2.1.0^{2,4}]octane.

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