

AN ABSTRACT OF THE THESIS OF

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Title: The Photodecomposition of t-butyl Bicyclo[7.1.0]decane-2-

percarboxylate

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Abstract approved:

Richard W. Thies

This paper describes the synthesis of t-butyl bicyclo[7.1.0]decane-2-percarboxylate and its photolytic decomposition. The title compound was found to undergo simple homolytic cleavage when exposed to light of 2537 Å; producing the cyclodecyl radical, carbon dioxide, and t-butoxy radical. The largest percentage of products arose from an intimate radical pair in a solvent cage. One product was postulated from a solvent separated radical pair; the remaining products from non-cage reactions. The short-lived cyclodecyl radical proceeded under thermodynamic control to give a predominance of cis olefin products rather than the expected equal ratio of cis-trans olefins that would normally be expected from a classical free radical reaction. No evidence for a cyclopropyl carbinyl nonclassical radical was observed.

The Photodecomposition of t-butyl  
Bicyclo[7.1.0]decane-2-percarboxylate

by

Donna Louise McRitchie

A THESIS

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"I got by - with a little help from my friends."

## TABLE OF CONTENTS

I.	Introduction .....	1
II.	Results .....	5
	Attempted preparation of the <u>syn</u> epimer of (XVI) .....	9
	Products of the decomposition of t-butyl bicyclo[7.1.0] decane-2-percarboxylate (VIII) .....	11
	Stability of cycloalkenes .....	18
	Effect of varying the method of decomposition .....	18
	Effect of solvent variation .....	19
III.	Discussion .....	20
	Products of the photolysis of t-butyl bicyclo[7.1.0] decane-2-percarboxylate (VIII) in pentane .....	20
	Effect of solvent .....	24
	The stereochemistry of cyclodecene formation .....	24
IV.	Experimental .....	30
	General information .....	30
	Preparative detail .....	31
	Preparation of 9,9-Dibromobicyclo[6.1.0]nonane (IX) ....	31
	Preparation of 1,2-Cyclononadiene (X) .....	31
	Preparation of cis-cyclononen-3-ol (XI) .....	32
	Preparation of cis-3-bromocyclononene (XII) .....	33
	Preparation of cis-3-cyanocyclononene (XIII) .....	33
	Preparation of methyl cyclononene-3-carboxylate (XIV) ..	34

Preparation of methyl bicyclo[7.1.0]decane-2-carboxylate (XV) .....	35
Preparation of bicyclo[7.1.0]decane-2-carboxylic acid (XVI) .....	36
Preparation of bicyclo[7.1.0]decane-2-carboxylic acid chloride (XVII) .....	37
Preparation of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII) .....	38
Method A .....	38
Method B .....	39
Preparation of methyl bicyclo[7.1.0]decane-2-ketone (XXI) .....	40
Preparation of bicyclo[7.1.0]decane-2-acetate (XXII).....	40
Preparation of cis-1-trimethylsiloxymethyl-2-cyclononene (XXIV) .....	41
Preparation of 2-trimethylsiloxymethylbicyclo[7.1.0]decane (XXVI) .....	42
Preparation of cis-cyclodecene .....	43
Attempted preparation of 2-bromobicyclo[7.1.0]decane (XX) .....	43
Preparation of trans-cyclodecene .....	44
Attempted preparation of cyclononene-3-carboxylic acid (XVIII) .....	44
Attempted preparation of 2-methylidenebicyclo[7.1.0]decane .....	45
Photolysis .....	46
Group 1 - olefin fraction .....	47
Group 3 - ether fraction .....	47
Group 4 - composition unknown .....	48
Pyrolysis .....	48
Determination of olefin stability .....	48
Bibliography .....	50

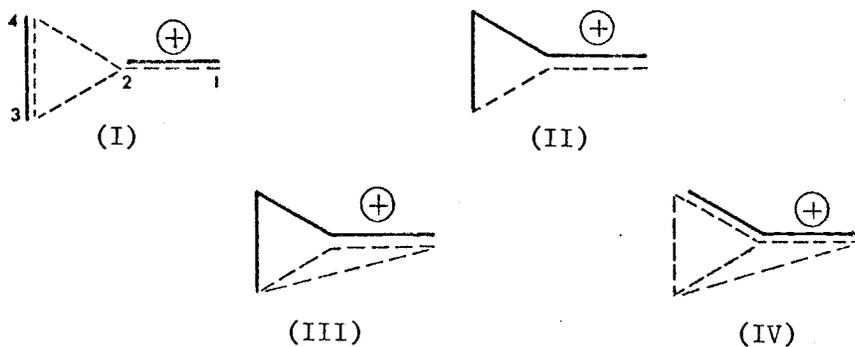
## TABLES

Table I.	Variation of product percentage with time .....	11
Table II.	Variation of <u>cis-trans</u> ratio with time .....	13
Table III.	Mass ratios of authentic <u>cis</u> -cyclodecene "A" and photolytically produced <u>cis</u> -cyclodecene "B" .....	14
Table IV.	Mass ratios of authentic <u>trans</u> -cyclodecene "A" and photolytically produced <u>trans</u> -cyclodecene "B" .....	15
Table V.	Results of mass spectral analysis .....	16
Table VI.	Major mass spectral fragments of group 4 .....	18
Table VII.	Variation of <u>trans</u> isomer with time .....	18

Photodecomposition of t-butyl Bicyclo[7.1.0]  
decane-2-percarboxylate

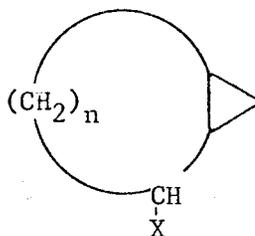
I. Introduction

Cyclopropyl carbinyll, homoallylic, and cyclobutyl carbonium ions and their interconversions have been the subject of many investigations in recent years. This study has led to a plethora of proposed intermediates with the symmetrical homoallylic or bisected ion (I), the homoallylic ion (II), and the bicyclobutonium ions (III) and (IV) being most commonly used.



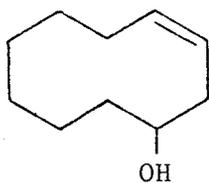
The result of a solvolysis proceeding via the intermediate cation (I), or a classical ion, should be the loss of stereochemistry at  $C_1$ . This has been demonstrated (11,24,34). Reactions proceeding via cations (II), (III), or (IV) should give products with stereochemistry at  $C_1$  retained.

Bicyclic compounds such as (V), where  $n=2, 3,$  or  $4$  give

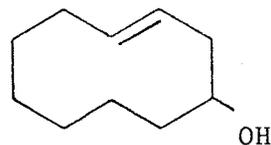


(V)

solvolysis products which show substantial loss of stereochemistry at the  $C_2$  position. In contrast, Winstein, et al. (17,28,29,42), demonstrated that for larger ring compounds (V) (where  $n= 5, 6,$  and  $7$ ) solvolysis products show retention of stereochemistry at  $C_2$ ; and they concluded that solvolysis had occurred via the nonclassical ions (II) and (III). The products, of acid catalyzed rearrangement of syn- and anti-bicyclo[7.1.0]decan-2-ol (V,  $n=6, X=OH$ ), or the solvolysis of the corresponding paranitrobenzoate (PNB) derivative (V,  $n=6, X=OPNB$ ), were dependent upon the stereochemistry of the starting material (29). The products of the solvolysis of both the syn and anti epimers retained stereochemistry at  $C_2$ . The products of the acid-catalyzed rearrangement showed stereoselective homoallylic isomerization; syn giving cis products (VI), and anti giving trans products (VII).



(VI)



(VII)

All observed products were consistent with the concerted involvement of the  $C_1-C_9$  cyclopropane  $\tau$  bond in delocalization of the charge on  $C_2$  (Figure 1).

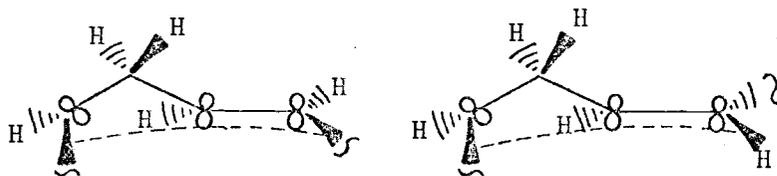
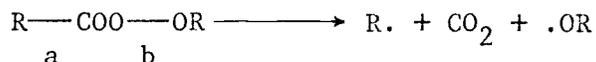


Figure 1

This study probes the corresponding cyclopropyl involvement at a radical center. Earlier studies demonstrated that cyclopropyl groups stabilize adjacent radicals (25) but the stereochemistry of the rearrangement to the homoallylic radical was not examined. Molecular orbital theory predicts less stabilization for the radical system than for the cation because the additional electron must go into an antibonding orbital. The delocalized radical intermediate, if formed, should retain the same stereospecific rearrangement as the cation, i.e., anti radical precursor would lead to a trans double bond. The alternative, a classical radical, should lose stereochemistry which would result in both cis and trans products.

Free radicals are commonly generated through hydrogen abstraction by another radical (41). This method was deemed unsuitable for our purposes since there is no control over the position or stereochemistry of attack. Formation of the cyclopropyl carbinyl radical by decomposition of a peroxyester allows generation of the radical at a specific position with a particular stereochemistry.

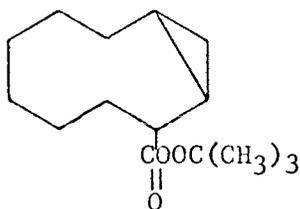
Photolytic decomposition of peroxyesters is a process widely accepted as proceeding via homolytic fragmentation.



The length of bonds (a) and (b) may not necessarily increase uniformly along the reaction coordinate. The character of these bonds in the transition state may vary (33), and there could very well be differences in the bond lengths due to differences between the syn and anti epimers. This can affect the kinetics of the reaction but should not be important in determining the products (36).

The ring strain, at least for medium sized rings, has little effect on thermal radical formation, and no appreciable influence of ring size has been reported for the decomposition of peroxyesters (33).

The t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII) was



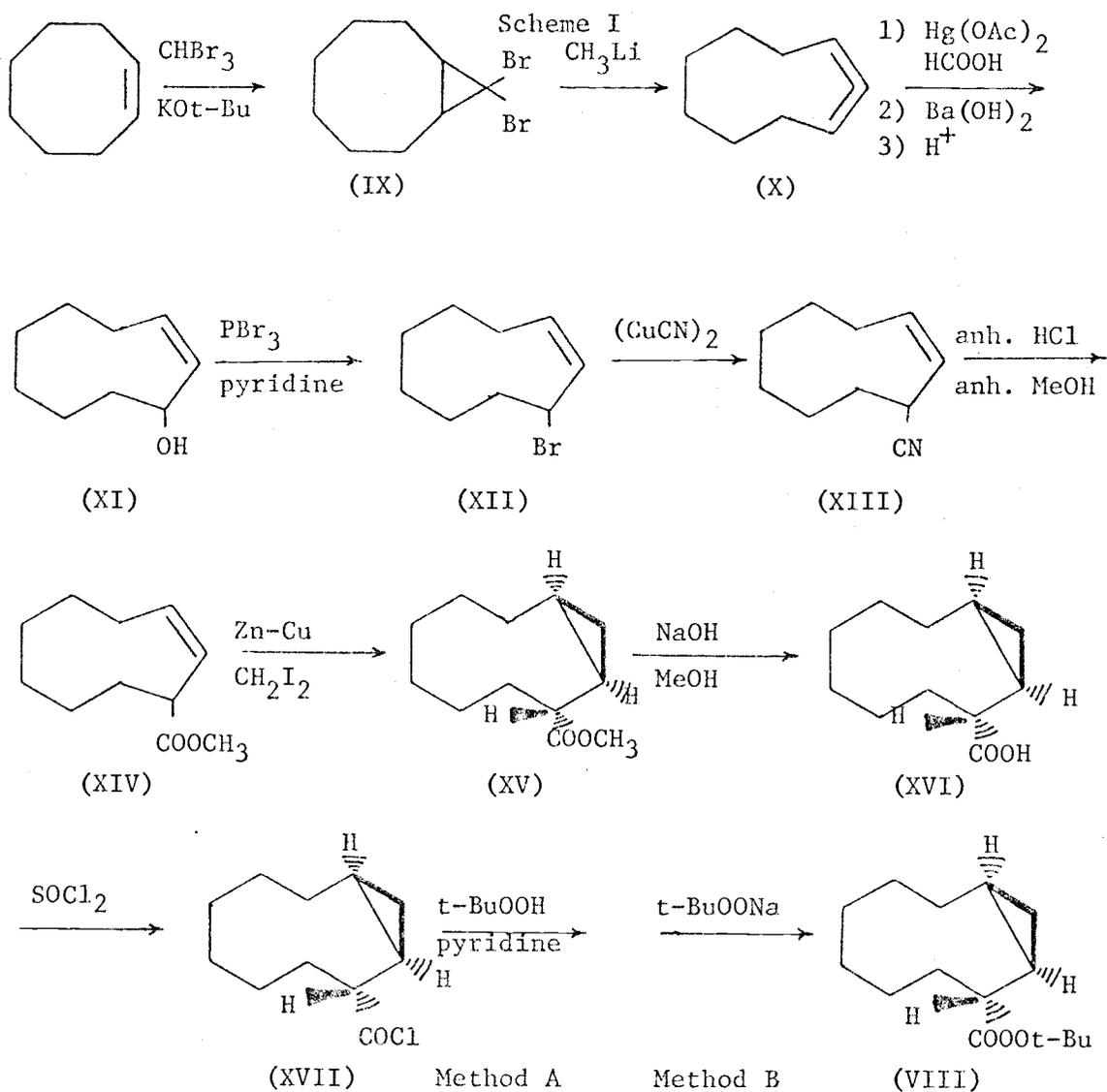
(VIII)

chosen as a suitable precursor to a cyclopropyl carbonyl radical. A comparison of the products obtained by photolytic generation of the bicyclo[7.1.0]decyl radical with the products obtained by solvolytic carbonium ion generation, should give useful information as to the nature of the reactive intermediates.

## II. Results

Preparation of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII)

The synthesis of peroxyester (VIII) from cis-cyclooctene was accomplished as shown in Scheme I. Preparation of the allylic



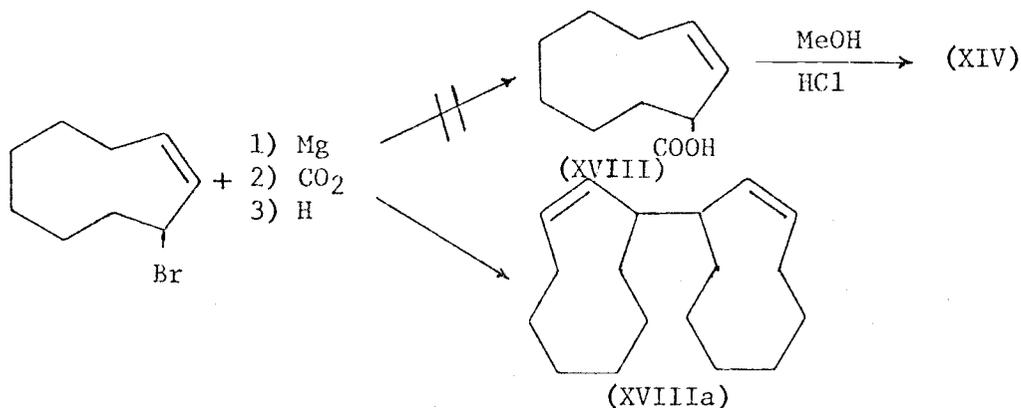
alcohol (XI) was carried out by the method of Skattebol (40), but with modifications to improve the overall yield. The bromide (XII) was prepared from alcohol (XI) with  $\text{PBr}_3$ ; the configuration of the olefin being retained during the course of the reaction. Reaction of the bromide (XII) with cuprous cyanide was difficult, with foaming occurring when the reaction was carried out in the absence of solvent, and in the presence of excess solvent, no reaction occurred. If the reaction had not begun after refluxing for 30 minutes, excess solvent was removed slowly with the use of a vigreux column and condenser until reaction was initiated. The nitrile (XIII) decomposed on heating in concentrated aqueous hydrochloric acid, and on dilution with methanol only the  $\alpha,\beta$ -unsaturated ester (carbonyl absorption  $1690\text{ cm}^{-1}$ ) was obtained in low yield. Hydrolysis of the nitrile under basic conditions also produced a low yield of conjugated ester. The nitrile could not be converted to the corresponding aldehyde when treated with lithium triethoxyaluminumhydride (8). Conversion of the nitrile to the methyl ester (XIV) was successfully accomplished by using a large excess of anhydrous methanol saturated with anhydrous hydrogen chloride. The conversion of the methyl ester (XIV) to the desired peroxyester (VIII) was achieved using the standard reactions shown in Scheme I.

The peroxyester (VIII) underwent vigorous exothermic decomposition upon heating above  $40\text{--}45^\circ\text{C}$  (all temperatures hereafter are Centigrade), making purification difficult. The compound was stored at or below  $-20^\circ$  as it decomposed slowly upon standing at room temperature. In early preparations of the peroxyester using Method A,

a small amount of t-butyl peroxide (NMR:  $\text{CCl}_4$ , singlet 1.15  $\delta$ ), and an anhydride (IR:  $1805\text{ cm}^{-1}$ ), were also formed. The anhydride impurity could not be removed, and to improve the purity of the peroxy-ester an alternative synthesis, Method B, was employed. This gave (VIII) free from anhydride and peroxide, but still containing unreacted t-butyl hydroperoxide, which could be readily removed by chromatography on Florisil.

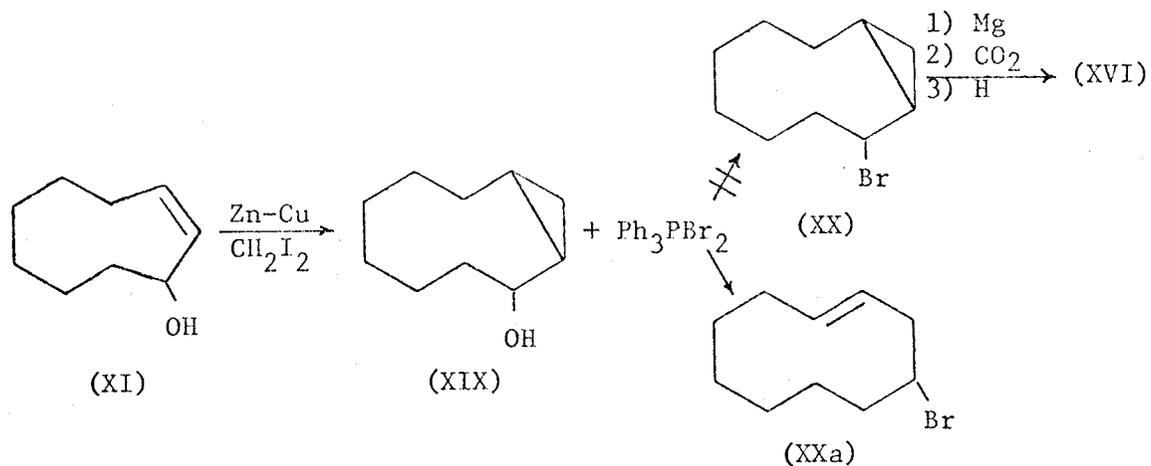
An alternate route to ester (XIV) from bromide (XII) (Scheme II) would have eliminated the difficult nitrile synthesis; however, the attempted preparation of the organomagnesium compound failed.

Scheme II



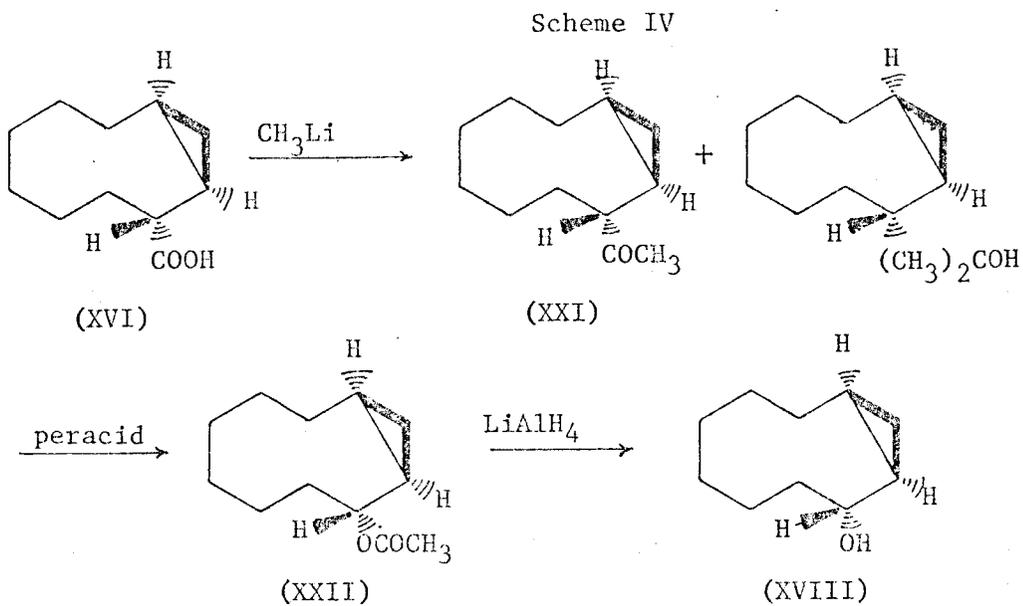
Scheme III outlines a modified route designed to avoid the coupling reaction.

Scheme III



This sequence was also unsuccessful inasmuch as replacement of the hydroxyl by bromide, using the mild brominating agent triphenylphosphine dibromide in dimethylformamide gave only rearranged bromide (XXa).

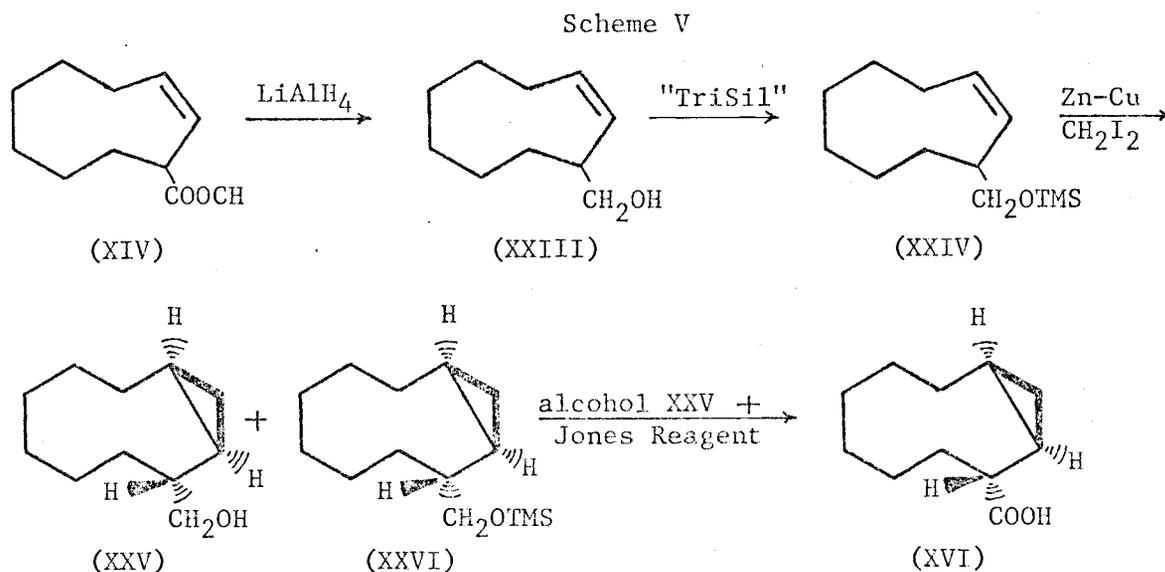
The configuration of the acid (XVI) was established by carrying out the series of reactions outlined in Scheme IV.



The Baeyer-Villiger reaction, a reaction producing acetates from methyl ketones, is known to proceed with retention of stereochemistry (21). Reaction of ketone (XXI) with *m*-chloroperbenzoic acid could, therefore, be expected to yield acetate (XXII) with the configuration at C<sub>2</sub> retained. The acetate (XXII) was isolated by preparative gc and reduced to the known alcohol anti (XIX). This demonstrated that the Simmons-Smith reaction on methyl ester (XIV) occurs with attack of the zinc-copper-methylene iodide complex trans to the methyl ester. This stereoselectivity may be due to the directing effect of the carbonyl group (a similar effect has been demonstrated (19,27,38)) or simply the result of a strong conformational preference.

Attempted preparation of the syn epimer of (XVI)

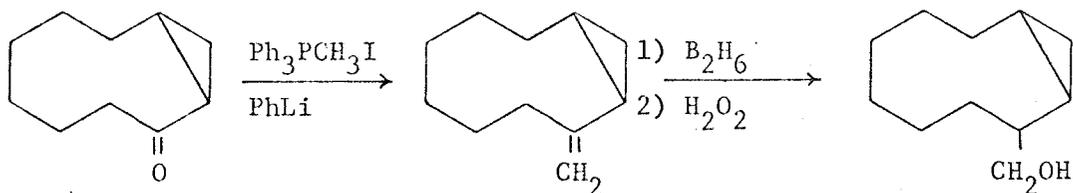
In an attempt to reduce any directing influence of the oxygen-containing substituents on the stereoselectivity of the Simmons-Smith reaction, and to obtain the syn epimer, the reactions outlined in Scheme V were carried out.



The Simmons-Smith reaction on the ether (XXIV) was rapid and gave a mixture of the ether (XXVI) and alcohol (XXV). These products were identical to the anti ether and alcohol obtained by reduction and silylation of ester (XV).

Several other preparations of the syn epimer were attempted. The ester (XV) could not be equilibrated in anhydrous methanol containing sodium methoxide. Reaction of the nitrile (XIII) with methylene iodide and zinc-copper couple (33) gave starting material, and a yellow gum with absorption in the infrared at  $2140\text{ cm}^{-1}$ . This contrasts with the normal position of CN absorption at  $2240\text{ cm}^{-1}$ . Preparation of the syn epimer via the Wittig reaction and subsequent oxidation (Scheme VI) was also unsuccessful.

Scheme VI



The ketone was unreactive to the triphenyl phosphonium methiodide, and only starting material was recovered. A solution of ester (XIV) in ethereal diazomethane was exposed to sunlight until the orange color of the diazomethane had disappeared, but only starting material was recovered.

Products of the decomposition of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII)

The decomposition of the peroxyester (VIII) was carried out both photolytically in pentane and cyclohexane, and thermally in pentane and cumene. The volatile decomposition products that eluted from column A (gc) in the first 30 minutes were of greatest interest (Figure II). Photolysis in pentane produced the highest yield of the cis- and trans-cyclodecene; hence reaction under these conditions was studied in the greatest detail. Photolysis of the peroxyester in pentane produced 19 major and 20 minor peaks (gc, column A). The minor peaks were not included in determining the product ratios. The progress of the peroxyester decomposition was followed at intervals during photolysis by examining the  $1770\text{ cm}^{-1}$  peak in the infrared spectrum (Table I).

TABLE I. VARIATION OF PRODUCT PERCENTAGE WITH TIME

Group	Retention Time <sup>a</sup>	10	Sample Time <sup>b</sup>		
			20	40	80
1. Olefins	5-8 minutes	3.7	9.2	14.2	15.5
2. c	c	2.0	2.8	1.4	1.5
3. Ether	14-17 minutes	11.5	9.6	11.8	13.0
4. d	17-19 minutes	14.5	20.6	27.2	32.0
5. Alcohol <sup>e</sup>	28-30 minutes	55.5	40.5	9.0	0
6. Dimers	after 50 minutes	11.5	17.7	36.4	38.0

a) From time of injection on column A.

b) In n-pentane.

c) Unknown, varied in time of elution as T-100° rose to T-140°.

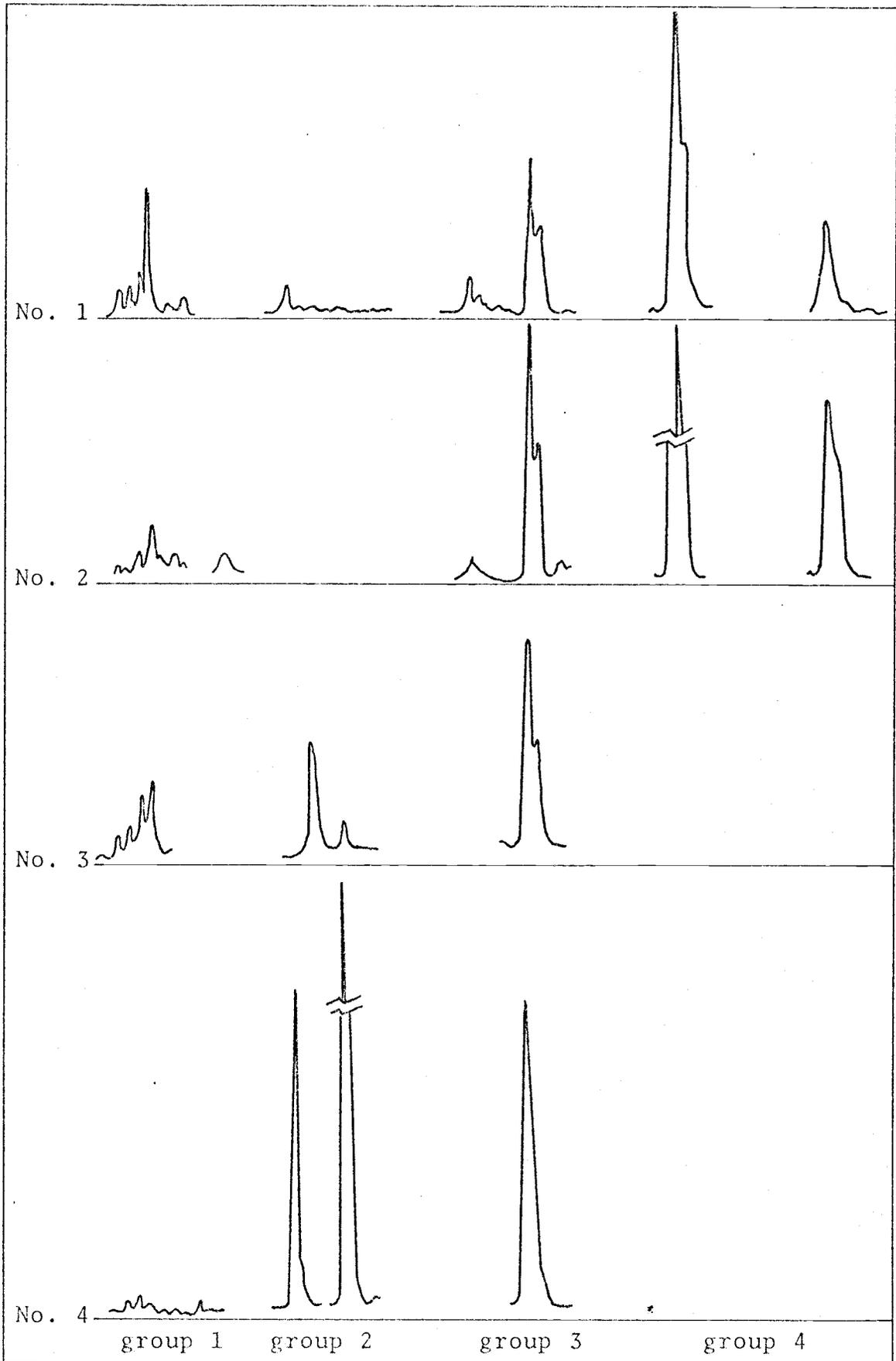
d) Thought to be a solvent-radical adduct.

e) From reduction of undecomposed peroxyester with LAH.

Figure II. Photolysis and Pyrolysis Products as Eluted on Column A.

- No. 1. Photolysis in Pentane
- No. 2. Pyrolysis in Pentane
- No. 3. Photolysis in Cyclohexane
- No. 4. Pyrolysis in Cumene

- Group 1. olefins
- Group 2. solvent dimers
- Group 3. ethers
- Group 4. solvent-radical adducts



Samples of peroxyester prepared by Method A (containing t-butyl peroxide and an anhydride as impurities) decomposed to yield only 11 major and 30-35 minor products. The difference was in the number of products of low volatility eluted after 30 minutes (gc, column A). Decompositions performed with these peroxyester samples produced the same spectrum of early retention time products as did pure peroxyester samples and were considered satisfactory for qualitative comparisons.

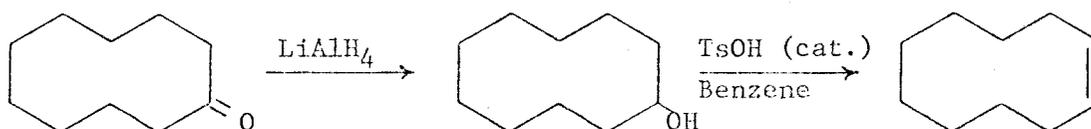
The products that eluted first, Group 1 (Figure II, No. 1 and Table I) were a mixture of six olefins. The composite infrared spectrum of this group resembles that of a mixture of authentic cis- and trans-cyclodecene. The cyclodecenes were 56% of Group 1. The ratio of peak heights for these isomeric olefins was measured and the variation during photolysis examined (Table II).

TABLE II. VARIATION OF cis-trans RATIO WITH TIME

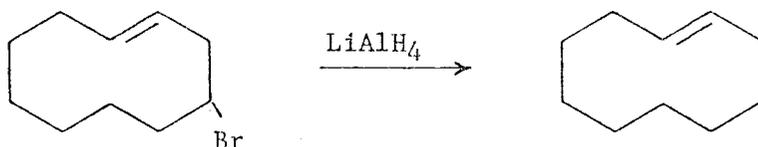
<u>Sample Time</u>	<u>cis:trans</u>	<u>% trans</u>
10 minutes	2.87	26
20 minutes	3.00	25
40 minutes	3.66	22
80 minutes	3.72	21

The isomeric cis-trans-cyclodecenes were identified on analytical gc by co-injection with authentic samples of the olefins prepared by alternative methods (Scheme VII). Identifications were further

Scheme VII



## Scheme VII (cont.)



substantiated by mass spectral analysis. The fragmentation pattern of the cis isomer was well resolved and its mass ratios could be compared to those obtained for an authentic sample of the cis-cyclodecene (Table III).

TABLE III. MASS RATIOS OF AUTHENTIC cis-CYCLODECENE "A" AND PHOTOLYTIALLY PRODUCED cis-CYCLODECENE "B"

<u>Mass</u>	<u>Olefin "A"</u>	<u>Olefin "B"</u>
138	.17	.18
110	.17	.18
109	.14	.13
97	.08	.09
96	.27	.27
95	.44	.41
83	.11	.09
82	.53	.45
81	.75	.77
80	.05	.09
79	.11	.18
77	.05	.09
69	.22	.13
68	.55	.50
67	1.00	1.00
66	.08	.09
65	.05	.09

Poor chromatographic resolution of trans-cyclodecene gave a mass spectrum contaminated by the preceding mass 136 olefins. Table IV compares the mass ratios of the photolysis product with authentic trans-cyclodecene. Significant contributions from mass 136 olefins are noted, and were identified by comparison with spectra of these olefins.

TABLE IV. MASS RATIOS OF AUTHENTIC trans-CYCLODECENE "A" AND PHOTOLYTICALLY PRODUCED trans-CYCLODECENE "B"

<u>Mass</u>	<u>Olefin "A"</u>	<u>Olefin "B"</u>	<u>Extra</u>
138	.11	.16	
121	-	.19	136 -15
110	.11	.16	
109	.10	.06	
108	-	.19	136 -28
107	-	.06	136 -29
97	.06	.03	
96	.17	.16	
95	.34	.50	
94	.02	.19	136 -42
93	.02	.16	136 -43
83	.07	.03	
82	.43	.47	
81	.71	.69	
80	.04	.19	136 -56
79	.07	.34	136 -57
77	.04	.16	136 -58
69	.20	.13	
68	.57	.44	
67	1.00	1.00	
66	.10	.19	
65	.06	.19	

The remaining olefins in Group 1 were unidentified; NMR and IR yielded few clues to their structures. The IR contained only C-H bending and stretching absorptions. The NMR indicated the presence of vinyl, allyl, -CH<sub>2</sub>- protons, and a multiplet at 0.87 $\delta$  which could be a methyl group.

The mass spectral data were important in assigning structure to the different products and are summarized in Table V. (Groups 1-4 are those illustrated in Figure II, their product ratios are listed in Table I.)

TABLE V. RESULTS OF MASS SPECTRAL ANALYSIS

<u>Group</u>	<u>Peak No.</u>	<u>% of Group<sup>a</sup></u>	<u>Parent Ion m/e</u>
1. Olefins	1	11	136
	2	11	138
	3	11	136
	4	45	138
	5	7	136
	6	15	(121) <sup>b</sup>
2. Unknown	1	100	c
3. Ethers	1	20	c
	2	80	210 <sup>d</sup>
4. Solvent- adducts	1	80	208
	2	20	208
5. Alcohol	1	e	168 <sup>f</sup>
6. Dimers	1	9	260
	2	91	274 <sup>g</sup>

- a) When photolysis was continued to complete disappearance of peroxyester.
- b) Largest mass peak found, no parent ion, fragmentation pattern similar to mass 136 olefins.
- c) Peak too small to give usable mass spectrum.
- d) Parent ion very small.
- e) Varied with time of photolysis, mass spectrum obtained on a short photolysis time sample.
- f) Lost water.
- g) Next prominent mass was 137.

On the basis of the composite IR and NMR data, and the mass of the parent ion, Group 3 (Figure II) was identified as a mixture of t-butyl ethers (both ring expanded, and unexpanded, Figure III).

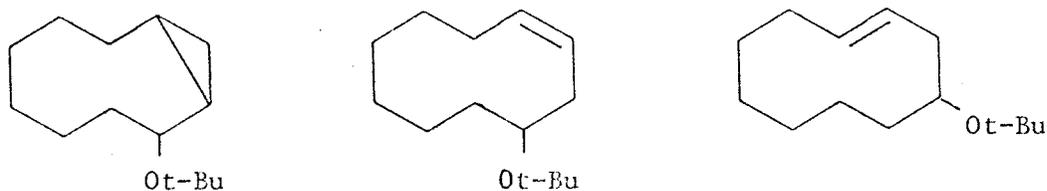
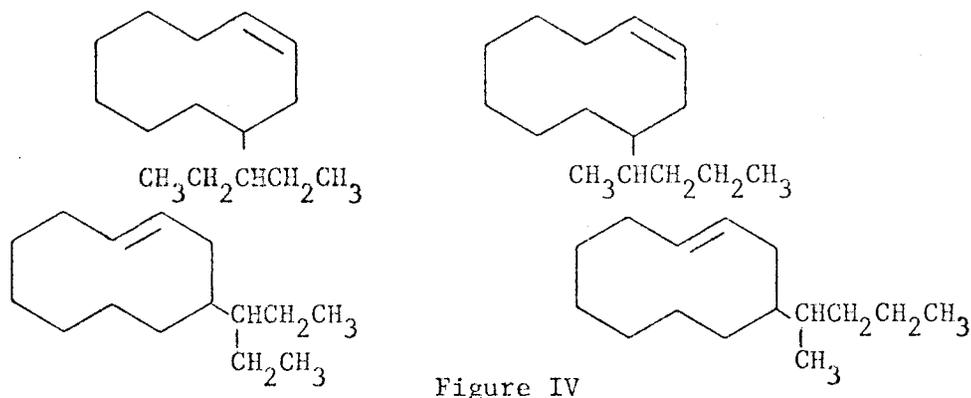


Figure III

Similarly, Group 4 (Figure II) was identified as a combination of ring expanded radicals with solvent radicals (Figure IV).



The long retention time products of Group 6 (not shown in Figure II) were identified as various dimers on the basis of the masses of the parent ions.

The two doublets of Group 4 were not well resolved even on column A. This column and column D were used in an attempt to obtain gc-mass spectra of the four individual compounds as additional support for the proposed structures (Figure IV). Too little material was eluted by column A to give good spectra, and the resolution on column D was only fair. With column D, however, the mass spectrometer sample was large enough to give measurable fragmentation peaks (Table VI).

TABLE VI. MAJOR MASS SPECTRAL FRAGMENTS OF GROUP 4

	Peak*	A	B	C	D**
207	(-H)	73	72	60	45
193	(-CH <sub>3</sub> )	6	5	4	2
179	(-C <sub>2</sub> H <sub>5</sub> )	26	51	29	53
165	(-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )	47	57	39	14
150	(-2C <sub>2</sub> H <sub>5</sub> )	8	15	8	6
137	(-C <sub>5</sub> H <sub>11</sub> )	106	107	104	105

\*Peak A first eluted, B its shoulder; Peak C next eluted, D its shoulder.

\*\*Spectrum intensity low. Measurements adjusted by a factor of 1.4 to be comparable to the three preceding peaks.

#### Stability of cycloalkenes

Photolysis of a solution in pentane containing 1% cis-cyclo-decene, and 1% of t-butyl peracetate showed no measurable isomeri-zation of the cis-cyclodecene in 60 minutes. However, a pentane solution containing 1% trans-4-trimethylsiloxycyclodecene, and 1% t-butyl peracetate was isomerized (Table VII).

TABLE VII. VARIATION OF trans ISOMER WITH TIME

<u>Time</u>	<u>% trans</u>
0 minutes	100
10 minutes	92
20 minutes	85
40 minutes	67

#### Effect of varying the method of decomposition

Pyrolysis of peroxyester (VIII) in pentane produced a reaction mixture (Figure II, No. 2) similar to that resulting from photolysis (Figure II, No. 1) but with the yield of olefins slightly reduced. After 60 minutes at 100° the ratio of cis- to trans-cyclo-decene was

found to be 2.61 (27.6% trans isomer). Products of the pyrolysis in cumene (Figure II, No. 4) were identified solely on the basis of their NMR spectra. The yield of olefins in this solvent was too small for our purposes and the other products were of little interest. The two large peaks shown in Group 2 (Figure II, No. 4) were bicumyl and cumyl t-butoxy ether respectively. The peak appearing with Group 3 was the same mixture of ethers as produced in all other decompositions.

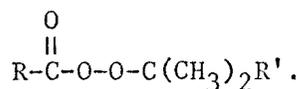
#### Effect of solvent variation

Photolysis of peroxyester (VIII) in cyclohexane produced the same olefins and ethers (Figure II, No. 3), but in addition a large peak that eluted in the Group 2 region. The mass spectrum of this product had a parent ion at mass 166 and a prominent peak at mass 83 which strongly suggests the solvent dimer bicyclohexyl. There were no products observed which could be attributed to a combination of cyclodecyl radical and solvent derived radicals (Figure II, Group 4). Decomposition in cumene also yielded solvent dimer, but no cyclodecyl radical-solvent radical products.

## III. Discussion

Products of the photolysis of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII) in pentane

Sheldon and Kochi (36) examined the decomposition products of a series of simple aliphatic peroxyesters of structure:



They found that all of the products fit into five categories:

- 1) RH and R'H,
- 2) R(-H) and R'(-H),
- 3) R'(CH<sub>3</sub>)<sub>2</sub>COH and/or (CH<sub>3</sub>)<sub>2</sub>C=O,
- 4) R'(CH<sub>3</sub>)<sub>2</sub>COR, and
- 5) R-R, R-R', and R'-R'.

The products in categories 2, 3, and 4 reportedly arose from reaction in a solvent cage via recombination of the alkyl and alkoxy radicals followed by disproportionation to alcohol and olefin. The products of the photolytic decomposition of peroxyester anti-(VIII), where R = cyclodecyl and R' = methyl, fit into the above categories.

The cis- and trans-cyclodecenes are the RH products and the remaining olefins in Group 1 are the R(-H) products. Authentic bicyclo[7.1.0]decane had the same retention time as trans-cyclodecene, but showed no parent ion, and an appreciable P-15 peak, and was not present in appreciable amounts. Group 1 peaks of molecular weight 136

(R(-H)) could be any one of a number of structures. One possible group of structures are the isomeric cyclodecadienes, excluding the 1,3-dienes which are not stable to photolysis conditions (10). A second group, the octalins, which could be formed by trans-annular bridging, lack distinctive functional characteristics and were in keeping with the spectral data. Products arising from opening of one of the outer cyclopropane bonds are a third possibility. An authentic sample of 3-methylcycloheptene had a shorter retention time (5.2 minutes on column A) than did the olefins in Group 1 which began eluting at about 7.8 minutes. Bicyclo[7.1.0]decenes could have formed if hydrogen abstraction occurred prior to opening of the cyclopropane ring. No appreciable amount of either bicyclo[7.1.0]decene or bicyclo[7.1.0]decane could have been present in Group 1 as no upfield cyclopropyl protons were detected in the composite NMR spectrum of this group.

The last peak of Group 1 had no molecular ion. The largest fragment in the spectrum had a mass of 121. The mass spectra of the mass 136 olefins show definite mass 121 fragments. It appears most likely that this last peak should also have a molecular weight of 136 making it another R(-H) product.

The second group of products large enough to be isolated and examined were the peaks of Group 3 (Figure II, No. 1). The composite spectrum indicated the presence of cyclopropyl protons, t-butyl, or t-butoxy groups, vinyl, and allyl protons. The IR indicated a C-O-C linkage. The molecular ion peak was very small but was identified at 210. These data support a mixture of t-butyl ethers, both ring-expanded,

and ring unexpanded. This identification is consistent with the category  $R'(CH_3)_2COR$  shown earlier, and the cage recombination mechanism could be proposed for its formation. However, there was some doubt as to the origin of these ethers. Their percentage of the observable product does not change with time (Table I). A small amount of material with a similar retention time was produced when the peroxyester was reduced with lithium aluminum hydride. The ether could have been produced from thermal decomposition of perester by the heat generated during reduction, or it may have been present in the peroxyester as an impurity which would have been spectrally (both IR and NMR) undetectable.

Assorted dimeric materials at retention times (gc) over 30 minutes were observed (Table IV); a completion of the resemblance of our photolysis products to those of Sheldon and Kochi. These dimers are non-cage reaction products. It is reasonable to assume that the similarity in products of this study to that of Sheldon and Kochi is due to the same reaction pathway, and that both sets of products arose primarily from reaction within a solvent cage. The proportion of dimeric materials in our product mixture was higher than that observed by Sheldon and Kochi. There are several factors that could account for this; however, two of primary importance are the viscosity of pentane, which decreases its efficiency as a cage solvent, and the stability of the radical which lengthens its lifetime sufficiently to allow more time for diffusion.

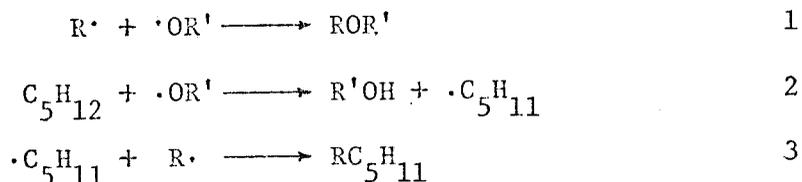
There is no analogy in the work of Sheldon and Kochi for the pair of doublets isolated as Group 4 (Figure II, No. 1). These peaks were identified mainly on the basis of the mass of the molecular ion,

208. Composite spectra showed no functionality other than vinyl protons, and terminal methyl group. These peaks appear to be the products of combination of cis- and trans-cyclodecyl radicals with 2- and 3-pentyl radicals. A single elemental analysis was obtained on a 5 mg sample collected by preparative gc on column E. The C-H analysis accounted for 91% of the molecule. The sample may have been contaminated with some of the column E stationary phase making the analysis useless. The inability to separate the individual components further hampered positive identification of these compounds. Group 4 was a higher percentage of the total observable product when the peroxyester was pyrolyzed at 100° in pentane (compare No. 1 with No. 2 in Figure II). Fragmentation of t-butoxy radical is generally enhanced by pyrolytic conditions. The new radicals produced are less stable and more likely to attack solvent, enhancing the concentration of pentyl radicals in the cage.

Photolysis of the peroxyester in cyclohexane produced no compounds resembling Group 4 (Figure II, No. 3) which supports the above structure assignment. That solvent radicals were still formed was demonstrated by the isolation of a Group 2 fraction and its subsequent identification as bicyclohexyl. When the decomposition was done thermally in cumene, Group 4 was again not present, while bicumyl was isolated in Group 2 (Figure II, No. 4).

The formation of the compounds in Group 4 was most likely the result of t-butoxy radical abstracting hydrogen from solvent, rather than recombining with the cyclodecyl radical. That the bicyclo[7.1.0]decyl radical diffuses easily from the pentane cage

is indicated by the higher quantity of dimer observed. The reactions:



must, then, occur simultaneously, as 2 and 3 from a solvent separated radical pair, and 3 from an intimate radical pair.

#### Effect of solvent

The reason for studying the photolysis in pentane was the higher yield of the cyclodecenes leading to some evaluation of the reaction intermediates. Figure II indicates that the type of products remains the same regardless of the method of decomposition. The significant difference between decomposition in pentane, and decomposition in cyclohexane and cumene, is the complete disappearance of Group 4, and the appearance of solvent dimer. There is no apparent explanation for this observation.

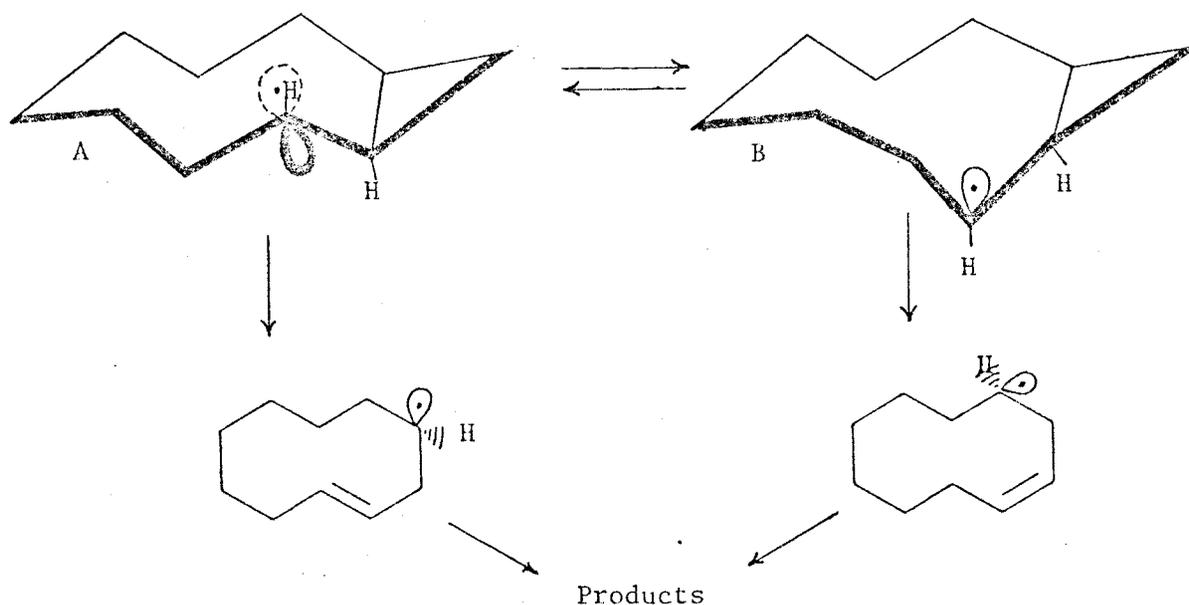
No attempt was made to compare the percentages of the products in different solvents since the purpose of the investigation was an observation of the stereochemical outcome of the decomposition.

#### The stereochemistry of cyclodecene formation

The preferential formation of the cis olefin by the anti epimer was not expected. This indicated that there was little or no radical delocalization by cyclopropane. Unlike the bicyclodecyl[7.1.0] carbonium ion, the radical can not hold stereochemistry, and both cis

and trans products are formed. The preponderance of the cis-cyclodecene over the trans isomer is not the result of rapid photochemical isomerization although some of the trans olefin was converted to the more stable cis olefin during photolysis. The isomerization was most likely sensitized by some remaining carbonyl species. During the first ten minutes of photolysis the cis-trans olefin ratio was 2.87. After pyrolysis at 100° in pentane for one hour, a cis-trans ratio of 2.61 was observed. Trans-cyclodecene is stable up to 300°. If the 2.61 ratio produced by pyrolytic decomposition represents the ratio which should be obtained if trans-cyclodecene was stable to the conditions of photolytic decomposition, the decrease in the amount of trans olefin product in the first ten minutes must be 10%. In a separate study on a pure trans olefin, the decrease in the ratio during the first ten minutes was 8%. This is consistent within the limits of accuracy of the method used to determine the ratios. Pyrolysis at 100°, in contrast with photolysis at 30°, would possibly produce a lower cis-trans ratio due to the shortened radical lifetime at the higher temperature. The olefin ratios obtained by the two different methods of decomposition are consistent since the same products were observed (Figure II, No. 1 and 2). Others (35) have demonstrated that peroxyesters undergoing simple homolytic cleavage produce essentially the same products by either photolytic or pyrolytic decomposition. The major differences observed were further fragmentation of the alkoxy radical at the higher temperatures usually employed for pyrolysis. Further fragmentation of the t-butoxy radical would lead to acetone and methane, neither of which was measured.

Models show that the geometry of peroxyester anti-(VIII) with the fewest unfavorable non-bonded interactions is a chair-like conformation with the bulky peroxyester group anti to cyclopropane and equatorial. The cis-cyclodecene was apparently formed by a rapid equilibrium of the cyclopropyl carbinyl radical generated by homolytic cleavage.



This is in contrast to the work of Beckwith and Phillipou (5) and others (14) who have shown that in rigid systems such as the  $3\beta$ , 5-cyclocholestan-6-yl radical, the cyclopropane bond which opens is that which is coplanar with the radical orbital. They observed products determined primarily by the stereochemistry of the starting material, and concluded that the classical cholesteryl radical was the intermediate. The origin of the trans products observed is clearly conformation A, whereas B should lead to the cis isomer. The latter is more stable by 2.2 kcal./mol, but the radical lifetime is apparently too short to reach the true thermodynamic equilibrium (12:1 at 100° in acetic acid) (12).

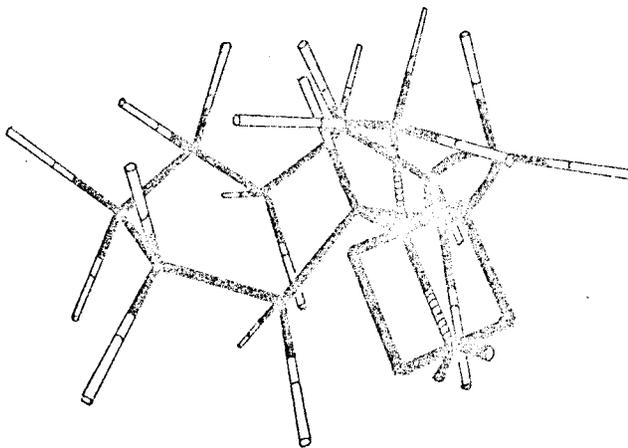
In passing from conformation A to conformation B the orbital containing the free electron would, at some point, be coplanar with the external cyclopropane bond. No products were observed which would correspond with external cyclopropane bond cleavage. Poulter and Winstein (29) have suggested that rings of this size may even twist into unfavorable conformations to utilize the more substituted arm of a cyclopropyl ring during ionization, thus avoiding a primary carbonium ion. Neither solvolysis nor acid catalyzed rearrangements of the bicyclodecyl carbonium ions was observed to give products arising from external bond cleavage. Crandall et al. (13) examined the products arising from the photolysis of bicyclo[6.1.0]nonan-3-one and found that the cyclopropyl carbonyl diradical yielded 86-90% of products arising from internal bond cleavage.

External bond cleavage by the bicyclodecyl radical to give a primary radical is clearly a higher energy pathway than that leading to trans-cyclodecene. The differences are apparently great enough to exclude this pathway to any appreciable extent.

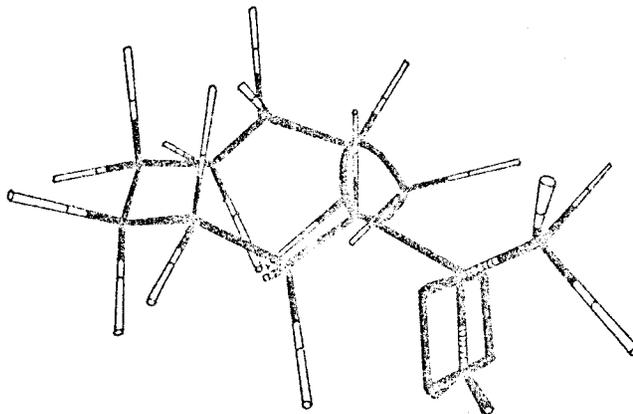
The inability to produce the syn epimer was unfortunate. If the cyclopropyl carbonyl radical is indeed in equilibrium between the syn and anti forms, with the syn-cis lower energy form predominating, then the pure syn epimer should produce a similar cis-trans ratio.

The stereoselectivity of the Simmons-Smith reaction on methyl ester (XIV) could have been either a conformational preference, or a directing effect of carbonyl oxygen. This stereoselectivity was not reduced in the trimethylsiloxy ethers (XXIV) which would seem to favor

the conformational preference argument. Models show that the conformation of the anti epimer with the fewest unfavorable non-bonded interactions can be represented as



However, models of the syn epimer appear crowded.



The unfavorable non-bonded interactions and crowding in the syn epimer would make equilibration with ethoxide ion an energetically unfavorable reaction, which may explain its failure.

The decomposition of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII) proceeds via homolytic cleavage in a solvent cage. The cyclodecyl radical intermediate equilibrates rapidly to the more thermodynamically stable configuration and then proceeds to products. One of the products appears to have been formed from a solvent separated

radical pair, analogous to that seen in carbonium ion solvolyses. The failure to positively identify these products, and the failure of other solvents to show a similar product, cloud this picture. In the ten-membered ring system, the cyclopropyl carbinyl carbonium ion, and the cyclopropyl carbinyl free radical yield olefinic products of opposite stereochemistry when generated from the same beginning epimer.

#### IV. Experimental

##### General information

The infrared spectra were measured on a Beckman IR-8 or a Perkin-Elmer Model 621. NMR spectra were measured on a Varian Associates HA-100 instrument. Mass spectra were obtained on a Varian MAT CH7 mass spectrometer. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories. Analytical gas-liquid chromatography (gc) utilized a Varian Model 1200 with flame ionization detector. The following columns were used:

Column A: 0.01 inch x 125 feet, Ucon Polar LB550X capillary;

Column B: 0.01 inch x 75 feet, Diethylene glycol succinate, capillary;

Column C: 0.01 inch x 100 feet, Apiezon N capillary;

Column D: 1/8 inch x 15 feet, 5% SF-96 on 110/120 Anachrom.

Flow through capillary columns was approximately 2 ml/min. The temperatures used ranged from 100° to 180°C. The flow through the 1/8 inch column was normally 25 ml/min at a temperature of 140°C.

Gas chromatographic separation with collection was accomplished on a Varian Model A-90 instrument equipped with:

Column E: 1/4 inch x 6 feet, 33% SF-96 on 80/90 Chromasorb A.

Photolysis was done in a Rayonet Photochemical Reactor Model No. RPR-100 (The Southern New England Ultraviolet Company).

Preparative detailPreparation of 9,9-Dibromobicyclo[6.1.0]nonane (IX)

In a typical preparation a mixture of 110 grams of cyclooctene, 50 grams of potassium tert-butoxide, and 300 ml of dried, distilled pentane was cooled in an ice bath under a nitrogen atmosphere. Stirring was maintained by a constant speed stirrer while a solution of 114 grams of bromoform in 50 ml of pentane was added. The addition required three hours, after which the mixture was allowed to warm to room temperature and was stirred for an additional four hours. The mixture was filtered, the filter cake washed with additional pentane and discarded. The combined filtrates were washed with water and dried over anhydrous magnesium sulfate. The bulk of the pentane was removed on a rotary evaporator and the crude product distilled under vacuum to yield 9,9-dibromobicyclo[6.1.0]nonane (100 g, 80%) bp 98°/1 mm. The IR and NMR were consistent with the product described by Skattebol (40).

Preparation of 1,2-Cyclononadiene (X)

A solution of (IX), 140 grams, in 400 ml of anhydrous ether was stirred under an inert atmosphere, while 250 ml of 2M methyl-lithium was added dropwise. The addition required two hours and the reaction mixture was maintained at -40°C with an acetone-dry ice bath. When addition had been completed the cooling bath was removed and the thick mass stirred at room temperature for an additional two hours. Distilled water was added dropwise with continued stirring until any excess of methyl-lithium had been destroyed. The ether layer was separated and the aqueous phase extracted with additional ether and

discarded. The combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. Upon distilling the residue under vacuum, 1,2-cyclononadiene was obtained (96 grams, 88%) bp 80-82°/28 mm. The IR spectrum was consistent with the compound described by Skattebol (40).

#### Preparation of cis-cyclononen-3-ol (XI)

To a solution of 5.1 grams of mercuric acetate in 500 ml of 88% formic acid was added 61 grams of 1,2-cyclononadiene. The solution was stirred by means of a magnetic stirrer for 14 hours at room temperature. The dark mixture was emulsified with 500 ml of ether by stirring vigorously, and the emulsion was poured over a liter of crushed ice. The ether layer was separated and washed successively with 3x150 ml of 5% sodium carbonate, 3x150 ml of distilled water, and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the crude product saponified without further purification.

The crude formate was mixed with 125 grams of hydrated barium hydroxide and 400 ml of water, and heated under reflux for four hours. After cooling the mixture was extracted with 2x125 ml portions of ether. The aqueous phase was made slightly acid with dilute hydrochloric acid and extracted with an additional 100 ml of ether. The combined ether extracts were washed successively with 1x50 ml of 1% hydrochloric acid and 2x100 ml of water, and dried over anhydrous sodium sulfate. The ether was removed on a rotary evaporator and the residue distilled under reduced pressure to yield cis-cyclononen-3-ol (90 grams, 83%) bp 72°/0.5 mm. IR (neat) 740  $\text{cm}^{-1}$  (cis olefin), 3350  $\text{cm}^{-1}$  (OH) and absence

of carbonyl absorptions. NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.3 (m,10); 1.9 (m,2); 3.8 (m,1); 4.3 (OH,m,1); 5.3 (septuplet,2). (Data were consistent with previous preparations of this compound by slightly different procedures) (40).

#### Preparation of cis-3-bromocyclononene (XII)

A solution containing 16.8 grams of cis-3-cyclononenol, 60 ml of dry ether, and 1.0 gram of dry pyridine was cooled in an ice bath under dry nitrogen atmosphere. To the cooled solution was added, with stirring, a solution of 10.4 grams of phosphorus tribromide in 50 ml of dry ether. The addition required 30 minutes, after which the ice bath was removed and the solution stirred at room temperature an additional four hours. The mixture was poured into 100 ml of ice water and the ether layer separated and washed successively with 3x50 ml of cold 5% sodium carbonate and 3x50 ml of cold water and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the resulting crude yellow liquid distilled under reduced pressure to yield cis-3-bromocyclononene as a colorless liquid (22.7 grams, 93%) bp  $54^\circ/0.4$  mm. IR (neat)  $740\text{ cm}^{-1}$  (cis olefin),  $690\text{ cm}^{-1}$  (C-Br), and absence of OH at  $3350\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.4 (m,6); 1.7 (m,2); 2.1 (m,4); 4.9 (m,1); 5.5 (m,2). Anal. calculated for  $\text{C}_9\text{H}_{15}\text{Br}$ : C, 53.21; H, 7.42. Found: C, 53.05; H, 7.61.

#### Preparation of cis-3-cyanocyclononene (XIII)

In a typical preparation, 10 grams of cis-3-bromocyclononene was mixed with 4.7 grams of cuprous cyanide and 20 ml of cyclohexane in a 250 ml flask equipped with an efficient reflux condenser and a

mechanical stirrer. The mixture was heated in an oil bath until steady reflux occurred. Heating was continued until evidence of reaction was apparent. Much heating and foaming occurred as the reaction began, and heating was discontinued when reaction became too vigorous. After the reaction had been initiated, refluxing was continued until the cuprous cyanide had changed from pale green to orange yellow. The mass was cooled with continued stirring and 50 ml additional cyclohexane were added. The mixture was stirred vigorously overnight at room temperature.<sup>1</sup> The solid was separated by filtration and washed with additional cyclohexane. The combined organic phase was diluted with an equal volume of ether and decanted from a yellow gum. The solvent was removed on a rotary evaporator and the residual oil distilled under vacuum to yield cis-3-cyanocyclononene, (5.6 grams, 75%) bp 69-70° at 0.5 mm. IR (neat) 735  $\text{cm}^{-1}$  (cis olefin), 2240  $\text{cm}^{-1}$  (CN), and the absence of OH and C-Br. NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.5 and 2.1 (m,12); 3.5 (sextuplet,1); 5.5 (septuplet,2). Anal. calculated for  $\text{C}_{10}\text{H}_{15}\text{N}$ : C, 80.50; H, 10.10. Found: C, 78.24 and 78.07, H, 9.90 and 10.02.

#### Preparation of methyl cyclononene-3-carboxylate (XIV)

Four hundred ml of dry AR methanol were chilled to 0° C and saturated with anhydrous hydrogen chloride. To this was added 29 grams of 3-cyanocyclononene. The solution was allowed to come to room temperature and was then warmed slowly until gentle reflux was

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<sup>1</sup>At this point the plastic insoluble mass sometimes hardened into a solid mass rather than a finely divided powder. The solid was transferred to a mortar and ground with additional solvent before filtration.

observed. Refluxing was continued until the nitrile absorption at  $2240\text{ cm}^{-1}$  was no longer present in the infrared spectrum, usually about four hours. The solution was cooled, poured into 500 ml of saturated ammonium chloride solution and extracted with 3x100 ml of ether. The combined extracts were washed successively with 3x50 ml of saturated sodium bicarbonate solution, and 3x50 ml of water, and dried over anhydrous sodium sulfate. Solvent was removed with a rotary evaporator and the colorless residue distilled under vacuum to yield methyl cyclononene-3-carboxylate (32 grams, 90%), bp  $80^\circ/1\text{ mm}$ . The ester produced a single peak on column A when  $T-140^\circ$  at  $t-12.4$  minutes and on column D,  $T-140^\circ$ ,  $t-8.7$  minutes. IR (neat)  $730\text{ cm}^{-1}$  (cis olefin - intensity very weak),  $1725\text{ cm}^{-1}$  (carbonyl  $\beta,\gamma$ -unsaturated), and absence of CN at  $2240\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.5 and 2.1 (m,12); 3.46 (m,1); 3.57 (singlet,3); 5.0 (m,2). Anal. calculated for  $\text{C}_{11}\text{H}_{18}\text{O}_2$ : C, 72.40; H, 9.95. Found: C, 72.19; H, 9.99. (Analytical sample purified on column E.)

Preparation of methyl bicyclo[7.1.0]decane-2-carboxylate (XV)

A mixture of 31 grams of zinc-copper couple (22), 100 ml of anhydrous ether, and 40 grams of methylene iodide was refluxed under nitrogen for 30 minutes. To this was added 30 grams of methyl cyclononene-3-carboxylate in 125 ml of ether. The mixture was refluxed for an hour and then an additional 40 grams of methylene iodide in 40 ml of ether was added dropwise over a two hour period, while maintaining reflux. After this addition, the reaction was monitored by gc (column A) and found to be about 85% complete. An

additional two hours of reflux yielded essentially 100% conversion. The reaction was quenched at room temperature with 150 ml of saturated ammonium chloride solution. The ether layer was separated and washed successively with 1x50 ml of saturated ammonium chloride, 3x50 ml of 10% sodium carbonate solution, and 3x50 ml of water, and dried over anhydrous sodium sulfate. The ether was removed on a rotary evaporator and the resulting oil distilled under reduced pressure to yield methyl bicyclo[7.1.0]decane-2-carboxylate (29 grams, 90%), bp 78°/0.7 mm. The ester eluted as a single peak on columns A, B, and D indicating that a single isomer had been obtained. The ester was reduced with lithium aluminum hydride in ether solution and the TMS ether prepared from the resulting alcohol with TriSil Concentrate (Registered Trade Name of Pierce Chemical Company). The ether eluted as a single peak on columns A, B, C, and D. IR (neat) 1725  $\text{cm}^{-1}$  (carbonyl), 3060  $\text{cm}^{-1}$  (cyclopropyl), and the absence of the cis olefin absorption at 730  $\text{cm}^{-1}$ , NMR ( $\text{CCl}_4$ ,  $\delta$ ) -0.38 (m,1); 0.58 (m,4 - approximate); 1.2, 1.5, and 1.8 (m,12 - approximate); 3.3 (singlet,3). (The large multiplet extending from 0.58 to 1.8 ppm integrated for 16 protons with the approximate proportions estimated.) Anal. calculated for  $\text{C}_{12}\text{H}_{20}\text{O}_2$ : C, 73.42; H, 10.23. Found: C, 73.26; H, 10.32. (Analytical sample purified on column E.)

#### Preparation of bicyclo[7.1.0]decane-2-carboxylic acid (XVI)

A solution of 13.5 grams of the methyl ester (XV) in 50 ml of methanol was mixed with a solution containing 5 grams of sodium hydroxide dissolved in 50 ml of water, and heated under reflux for

one hour. The solution was cooled, diluted with an equal volume of water and extracted with 3x50 ml portions of ether. The aqueous phase was chilled and made strongly acid with 6M hydrochloric acid. The white crystalline solid was filtered, water washed, and dried. The crude acid melted 74-76°. Recrystallization from an ethanol-water mixture yielded bicyclo[7.1.0]decane-2-carboxylic acid (1x, 12.3 grams, 97%) mp 77-78° uncorrected (Fisher-Johns). IR (mull in Nujol and KBr pellet) 2700  $\text{cm}^{-1}$  (broad intense carboxylic acid OH); 1700  $\text{cm}^{-1}$  (carbonyl). NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.5 (m,12); -0.14 and 0.76 (m,1 and m,4); 11.14 (singlet,1). Anal. calculated for  $\text{C}_{11}\text{H}_{18}\text{O}_2$ : C, 72.40; H, 9.95. Found: C, 72.29; H, 9.97.

The acid was reduced with an ether solution of lithium aluminum hydride and the resulting alcohol treated with TriSil Concentrate. The resulting ether eluted as a single peak on columns A, B, C, and D. Co-injection of this ether with the ether obtained from ester (XV) produced only a single peak on column A. This demonstrated that the saponification conditions did not cause observable epimerization.

#### Preparation of bicyclo[7.1.0]decane-2-carboxylic acid chloride (XVII)

A solution of 5 grams of the carboxylic acid (XVI) in 5 ml of thionyl chloride was carefully heated to reflux temperature in an oil bath. When evolution of acid gases had stopped, usually within an hour or less, the excess thionyl chloride was removed with the aid of a water aspirator, and the residual yellow oil distilled under reduced pressure to yield the acid chloride as a colorless oil (5 grams, 90%) bp 66°/0.2 mm. IR (neat) 3060  $\text{cm}^{-1}$  (cyclopropyl); 1780

$\text{cm}^{-1}$  (carbonyl); and absence of OH at  $2700 \text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ,  $\delta$ )  $-0.02$  and  $0.78$  (m,1 and m,4);  $1.68$  (m,12);  $2.4$  (m,1).

Preparation of t-butyl bicyclo[7.1.0]decane-2-percarboxylate (VIII)

Method A

A solution containing 5 grams of acid chloride (XVII) and 3 grams of t-butyl hydroperoxide (Matheson, Coleman & Bell BX1975) in 75 ml of dry distilled pentane was cooled under nitrogen to  $-25^\circ\text{C}$  in an acetone dry-ice bath. A solution containing 2 ml of dry pyridine in 20 ml of pentane was added dropwise with stirring so as to maintain the temperature at  $-25^\circ$ . When addition was complete, the mixture was allowed to come to room temperature slowly. The reaction mixture was poured into 20 ml of ice cold 10% sulfuric acid with stirring and the pentane layer was separated. The organic phase was washed successively with 2x20 ml of 10% chilled sulfuric acid, 3x20 ml of chilled 10% sodium carbonate, 3x20 ml of ice water, and dried in the refrigerator<sup>2</sup> over anhydrous magnesium sulfate. The volume of the solution was reduced to roughly 20 ml on a rotary evaporator, and the solution was chromatographed on 100 grams of SilicAR. The resulting colorless oil weighed about 6 grams (90%). IR (neat)  $3060 \text{ cm}^{-1}$  (cyclopropyl);  $1770 \text{ cm}^{-1}$  (peroxy ester carbonyl - high intensity);  $1370$  and  $1390 \text{ cm}^{-1}$  (t-butyl group); and absence of OH in the  $3300\text{--}3500 \text{ cm}^{-1}$  region, but showing a carbonyl absorbance at  $1805 \text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ,  $\delta$ ) cyclopropyl protons at  $-0.15$  and  $0.85$  were well defined multiplets; t-butyl protons

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<sup>2</sup>Compound decomposes with perceptible force and evolution of considerable heat if allowed to warm over  $30\text{--}35^\circ\text{C}$ .

at 1.25 were a sharp singlet;  $\text{CH}_2$  protons were a large multiplet spread between 1.0 and 2.0. Integrations of the compounds prepared by this method were never in the proper proportions.

#### Method B

The sodium salt of *t*-butyl hydroperoxide was prepared according to the procedure outlined by Bartlett (4).

A suspension of 2.2 grams of sodium *t*-butyl peroxide in 20 ml of anhydrous ether was stirred and cooled to ice bath temperature, while 1.7 grams of acid chloride (XVII) in 10 ml of ether was added dropwise. The reaction was carried out under an inert atmosphere. When addition was complete, the mixture was allowed to come to room temperature and then 10 ml of distilled water was added and the mixture stirred vigorously for ten minutes. The mixture was diluted with 25 ml of pentane and the organic phase separated and washed with 3x20 ml cold 10% sulfuric acid, 3x20 ml of cold 10% sodium carbonate, 3x20 ml of cold water, and dried over anhydrous magnesium sulfate. The dried solution was filtered and reduced in volume on a rotary evaporator. The colorless residue had OH absorption near  $3500\text{ cm}^{-1}$  which was removed by chromatographing on 20 grams of Florisil using pentane as the solvent. The product, *t*-butyl bicyclo[7.1.0]decane-2-percarboxylate (1.1 grams, 50%). IR (neat)  $3060\text{ cm}^{-1}$  (cyclopropyl);  $1770\text{ cm}^{-1}$  (peroxyester carbonyl);  $1365$  and  $1387\text{ cm}^{-1}$  (*t*-butyl group); and absence of OH and extraneous carbonyl. NMR ( $\text{CCl}_4$ ,  $\delta$ ) appears to be identical with that of material prepared by Method A.<sup>3</sup> Peaks

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<sup>3</sup>Thanks are due Dr. W. S. Brey, Jr. for the spectrum and its integration, and the University of Florida for the use of the XL-100 instrument.

were integrated by use of a planimeter, giving cyclopropyl at -0.15 (m,1); 0.85 (m,4); t-butyl at 1.25 (singlet,9); and -CH<sub>2</sub>- at 1.0-2.0 (m,12).

Preparation of methyl bicyclo[7.1.0]decane-2-ketone (XXI)

A solution of 2.7 grams of the acid (XVI) in 5 ml of dry ether was stirred under a nitrogen atmosphere while 21 ml of a 1.8M methyl-lithium solution was added at a rate to maintain gentle reflux. When addition was complete a saturated solution of ammonium chloride was added dropwise with stirring and cooling until no further reaction was observed. The ether layer was separated and washed with water and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the resulting viscous oil was distilled under reduced pressure to yield methyl bicyclo[7.1.0]decane-2-ketone (2.2 grams, 80%) bp 75°/0.4 mm. Analytical gc on column A indicated approximately 20% contamination by the alcohol resulting from addition of a second molecule of methyllithium. When T-140° the ketone eluted at t-17 minutes, and the alcohol at t-22 minutes. IR (neat) 1700 cm<sup>-1</sup> (carbonyl); 3060 cm<sup>-1</sup> (cyclopropyl). Anal. calculated for C<sub>12</sub>H<sub>20</sub>O: C, 80.00; H, 11.18. Found: C, 80.20; H, 10.98. (Analytical sample prepared by chromatography on column E, T-150°.

Preparation of bicyclo[7.1.0]decane-2-acetate (XXII)

A solution containing 0.5 gram of ketone (XXI) in 5 ml of chloroform was mixed with 0.5 gram of m-chloroperbenzoic acid dissolved in 10 ml of chloroform. The solution was left in the dark for a week at room temperature. The m-chlorobenzoic acid which had precipitated

was finely divided and passed readily through the filter, so the chloroform was replaced with ether and the ether solution washed free of the acid with cold 1N sodium hydroxide. The acid free solution was washed further with 3x30 ml of cold water and 1x30 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Solvent was removed on a rotary evaporator and the residue purified by preparative chromatography on column E, T-180°, t-7 minutes. IR (neat) 3060  $\text{cm}^{-1}$  (cyclopropyl); 1725  $\text{cm}^{-1}$  (carbonyl; and 1245  $\text{cm}^{-1}$  (acetate ester). NMR ( $\text{CCl}_4$ ,  $\delta$ ) 0.05 and 0.70 (m,1 and m,4); 4.6 (m,1); 1.97 (singlet,3); 1.0-2.3 (broad multiplet with unexplained high integration). Anal. calculated for  $\text{C}_{12}\text{H}_{20}\text{O}_2$ : C, 73.42; H, 10.23. Found: C, 73.30; H, 10.11.

Preparation of cis-1-trimethylsiloxymethyl-2-cyclononene (XXIV)

One gram of methyl ester (XIV) dissolved in 5 ml of anhydrous ether was treated dropwise with an ethereal solution of lithium aluminum hydride until gas evolution had ceased. An additional five drops were added and then a ml of saturated ammonium chloride was added and the mixture stirred vigorously. The ether layer was separated and shaken with an additional 5 ml of saturated ammonium chloride solution and then dried over anhydrous magnesium sulfate. The dried ether solution was mixed with 4 ml of TriSil Concentrate and refluxed for one hour. The cooled solution was shaken vigorously with 2x10 ml portions of water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the colorless residue distilled at reduced pressure to yield cis-1-trimethylsiloxymethyl-2-

cyclononene (1.1 gram, 100%) bp  $73^{\circ}/0.5$  mm. Further purification was done by preparative gc using column E, T- $180^{\circ}$ , t-15 minutes. Analytical gc of the peak isolated on column E yielded a single peak on column A, T- $140^{\circ}$ , t-6 minutes. IR (neat)  $735\text{ cm}^{-1}$  (cis olefin-intensity very weak); absence of all carbonyl, hydroxyl, and carboxyl. NMR ( $\text{CCl}_4$ ,  $\delta$ ) 0.0 (singlet,9); 2.06 (m,2); 2.55 (m,1); 3.37 (m,2); 5.0-5.8 (m,2); and a large multiplet at 1.48 which integrated for 12 rather than 10 protons. Anal. calculated for  $\text{C}_{13}\text{H}_{26}\text{SiO}$ : C, 68.95; H, 11.57. Found: C, 69.43; H, 10.79. (Analytical sample prepared on column E, from which it eluted as a single peak.)

Preparation of 2-trimethylsiloxymethylbicyclo[7.1.0]decane (XXVI)

A mixture of 1.4 grams of zinc-copper couple (22), 5 ml of anhydrous ether, and 3 grams of methylene iodide were refluxed under nitrogen for 30 minutes. To the refluxing mixture was added 1.1 grams of the ether (XXIV) in 5 ml of anhydrous ether. After 30 minutes an additional 4 grams of methylene iodide in 5 ml of ether were added dropwise over a two hour period. The reaction was examined by gc and found to be complete. The reaction was quenched by addition of saturated ammonium chloride at  $0^{\circ}\text{C}$ . The ether layer was separated and washed successively with 3x50 ml of sodium carbonate solution, 3x50 ml of water, and dried over anhydrous sodium sulfate. Examination of the product on column A at T- $140^{\circ}$  showed two peaks at t-10 minutes and t-22 minutes. The ether was purified for analysis by preparative gc on column E. Anal. calculated for  $\text{C}_{14}\text{H}_{28}\text{SiO}$ : C, 69.93; H, 11.73. Found: C, 70.04; H, 11.57.

Preparation of cis-cyclodecene

A solution of 200 mg of cyclodecanone (Aldrich) in ether was treated dropwise with ethereal lithium aluminum hydride until no further gas evolution was observed. The mixture was shaken with 2x10 ml of saturated ammonium chloride solution, 2x10 ml of 1N hydrochloric acid, 2x10 ml of saturated sodium bicarbonate and 2x10 ml of water and dried over anhydrous sodium sulfate. Analytical gc on column D, T-140° showed a single peak at t-6 minutes. The solution was evaporated and benzene was added to the residue along with 200 mg of p-toluenesulfonic acid. The solution was refluxed on a Dean-Stark apparatus overnight and the acid removed by washing with saturated sodium bicarbonate. The solution was dried over anhydrous magnesium sulfate and the benzene removed on a rotary evaporator. Gc: column A, T-100°, t-6 minutes; column D, T-140°, t-2.5 minutes; purified on column E, T-150°, t-9 minutes. IR (neat)  $705\text{ cm}^{-1}$  (cis olefin), literature value  $697\text{ cm}^{-1}$  (8). NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.5 (m,12); 2.3 (m,4); 5.4 (m,2).

Attempted preparation of 2-bromobicyclo[7.1.0]decane (XX)

A mixture of 4 grams of bicyclo[7.1.0]decan-2-ol and 7.1 grams of triphenyl phosphine in 25 ml of dry, distilled, dimethylformamide was cooled in an ice bath and a solution of bromine in dimethylformamide was added dropwise until one drop caused a permanent yellow color. The resulting solution was distilled under reduced pressure until the distillate began to solidify. The oil which had been collected was diluted with ether and extracted with 5x50 ml of water and dried over

anhydrous sodium sulfate. The ether was evaporated and the yellow oil examined by IR. The cyclopropyl absorption at  $3060\text{ cm}^{-1}$  was no longer present, and the product had a strong trans olefin absorption at  $980\text{ cm}^{-1}$  and a diffuse band at  $680\text{--}700\text{ cm}^{-1}$  indicating probably CBr. The presence of Br was confirmed by a positive Beilstein test. The product appeared to be trans-bromocyclodecene rather than the desired bicyclic and no further purification was attempted.

#### Preparation of trans-cyclodecene

A sample of crude trans-3-bromocyclodecene was refluxed with an excess of ethereal lithium aluminum hydride for nearly 24 hours. The ether solution was washed successively with 2x25 ml of saturated ammonium chloride solution, 2x25 ml of 1N hydrochloric acid, and water until washings were neutral. After drying over anhydrous sodium sulfate the ether was removed on a rotary evaporator and the residue distilled under reduced pressure. A colorless liquid (0.4 ml, bp  $32\text{--}34^\circ/0.8\text{ mm}$ ) which gave a negative Beilstein test, was tentatively identified as trans-cyclodecene. Gc: column A,  $T\text{--}100^\circ$ ,  $t\text{--}5.6$  minutes (0.4 minutes shorter than the cis isomer which was present in minute amount). IR (neat)  $980\text{ cm}^{-1}$  (trans olefin, strong absorption); literature value for this isomer (8) was  $980\text{ cm}^{-1}$ . NMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.42 (m,12); 2.05 (m,4); 5.37 (m,2).

#### Attempted preparation of cyclononene-3-carboxylic acid (XVIII)

A mixture of 0.5 gram of magnesium turnings and 25 ml of anhydrous ether was stirred under nitrogen in a predried apparatus. A solution of 3-bromocyclononene in 25 ml of ether was added dropwise,

and the reaction began immediately. The rate of addition was adjusted to maintain steady reflux, and required about 20 minutes. The mixture was refluxed an additional two hours and cooled. Finely crushed dry ice weighing approximately 5 grams was added to the mixture with vigorous stirring and stirring was continued until the mixture had returned to room temperature. The thick mixture was added to 20 ml of cold 5% hydrochloric acid. The ether layer was separated from unreacted magnesium and the acid and washed with 2x10 ml of 5% hydrochloric acid, 3x20 ml of water, and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator leaving a white crystalline residue. The solid gave a negative Beilstein test, and its infrared spectrum contained only C-H absorption bands. The absence of carbonyl and carboxyl OH absorptions indicated that the desired reaction had not occurred.

The reaction was repeated using 150 ml of ether in an attempt to minimize the undesired reaction, but the same crystalline solid was obtained. The product was assumed to be two coupled cyclononene rings and no further purification or identification was attempted.

#### Attempted preparation of 2-methylidenebicyclo[7.1.0]decane

A solution of 2.5 ml of 2.2M phenyllithium in 70:30 benzene: ether was placed in a predried apparatus under a nitrogen atmosphere and a suspension of 2 grams of triphenylphosphonium methiodide in ether was added. The mixture was stirred for 30 minutes at room temperature and yielded a bright yellow solution and a thick mass of white solid. A solution of 0.7 gram of bicyclo[7.1.0]deca-2-none in ether was added and the mixture warmed to reflux. After heating under

reflux for 24 hours, no trace of any product could be detected on column B. Reaction was discontinued and 0.6 gram of ketone was recovered unchanged.

### Photolysis

Samples were prepared as 1% solutions in dry distilled solvent, pentane or cyclohexane, placed in a quartz tube equipped with a reflux condenser and flushed with dry nitrogen for ten minutes before beginning the photolysis. The apparatus was placed in the reactor and aliquots were withdrawn at 10, 20, 40, 60, and 80 minutes. The disappearance of the carbonyl peak at  $1770\text{ cm}^{-1}$  in the infrared spectrum was complete at 60 minutes. The solvent was removed on a rotary evaporator at room temperature and no effort was made to retain methane, acetone, t-butanol, or any other reaction product of high volatility. In a typical experiment 1.102 grams of the peroxyester yielded 0.808 gram of photolysis products, calculated for loss of  $\text{CO}_2$  only, 0.910 gram. Analytical gc was done on column A as follows: injection at  $T-100^\circ$  and elution for ten minutes followed by temperature programmed heating to  $T-140^\circ$  and elution for 22 minutes, then temperature programmed heating to  $T-180^\circ$  and elution until the column was cleared, usually an additional 35 minutes. Preparative gc was performed on column E at  $T-140^\circ$  on which the products eluted as five groups. Further analytical data could only be obtained on the groups of products as further separation into individual components was not possible. The percentages of the five groups, as listed in the discussion were obtained by cutting and weighing the peaks. To confirm that the products

examined were arising from the bicyclo[7.1.0]decyl radical, an 1% solution of t-butyl peroxide in pentane was subjected to the photolysis conditions for one hour. Examination of the products on column A showed no peaks eluting after t-3.5 minutes. All peroxyester photolysis products examined were retained at least five minutes under the same column conditions. Analytical data were obtained on the products of the photolysis in pentane. Only three of the five groups of compounds were obtained in sufficient quantity to attempt further analysis.

#### Group 1 - olefin fraction

The data on this group are on a composite of six peaks. IR (neat)  $980\text{ cm}^{-1}$  (trans olefin, intensity weak for this absorption);  $708\text{ cm}^{-1}$  (cis olefin, intensity stronger than trans); normal C-H bending and stretching frequencies. No other distinguishing features. NMR ( $\text{CCl}_4$ ,  $\delta$ ) 0.87 (multiplet, terminal methyl?); 1.48 (multiplet,  $-\text{CH}_2-$ ); 2.18 (multiplet, allylic protons); and 5.34 (multiplet, vinyl protons).

#### Group 3 - ether fraction

The data on this group are on two peaks, both doublets, in the ratio of 4:1. IR (neat)  $1048\text{ cm}^{-1}$  (C-O-C); 1192, 1358, and  $1382\text{ cm}^{-1}$  (t-butyl group); typical C-H bending and stretching bands and little perceptible unsaturation. NMR ( $\text{CCl}_4$ ,  $\delta$ ) -0.15 and 0.80 (multiplet, cyclopropyl); 1.08 (singlet, t-butyl or t-butoxy); 5.38 (multiplet, vinyl protons); 1.35 (broad multiplet  $-\text{CH}_2-$ , but with a shoulder at 2.0-2.1 that could be allylic protons); 3.1 (multiplet, unknown).

Group 4 - composition unknown

The data on this group are on two sets of doublets in the ratio of 2:1. IR (neat) C-H stretch 2820-2990  $\text{cm}^{-1}$ ; C-H bending 1440-1460  $\text{cm}^{-1}$ ; 1375  $\text{cm}^{-1}$  (very weak) terminal methyl (?); and no other bands. NMR ( $\text{CCl}_4$ ,  $\delta$ ) 0.86 (multiplet, possibly terminal methyl); 1.40 (multiplet,  $-\text{CH}_2-$ ); 2.0 and 2.48 (multiplets, possible two types of allylic protons); and 5.27 (multiplet, vinyl protons). Anal. Found: C, 79.52; H, 11.57; O, 8.91 (by difference).

Pyrolysis

A 1% solution of the peroxyester in pentane was sealed in a heavy walled ampule under nitrogen and dropped into a container of boiling water for one hour. The ampule was cooled quickly in ice, opened and treated with an ethereal solution of lithium aluminum hydride. Excess LAH was destroyed and the solution dried and analyzed on column A.

A 1% solution of the peroxyester in cumene (distilled) was refluxed under a stream of nitrogen for one hour and then cooled quickly. The samples were treated as described above and analyzed on column A.

Determination of olefin stability

A solution containing 1% of cis-cyclodecene and 1% of t-butyl peracetate in pentane was photolyzed until all carbonyl absorption had disappeared from the infrared spectrum. Aliquots taken at 10, 20, and 40 minutes were examined for isomerization on column A. No isomerization was observed.

A solution of 1% of trans-4-trimethylsiloxycyclodecene and 1% of t-butyl peracetate in pentane were treated in a similar manner. After 20 minutes the TMS compound begins to decompose to products other than cis isomers; however, the 10 and 20 minute samples were sufficient to establish that a rapid equilibration of products does not occur.

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