

AN ABSTRACT OF THE THESIS OF

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Title: OXYMERCURATION OF CYCLODECA-1, 2, 5, 8-TETRAENE

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Dr. Richard W. Thies

The reactions of cyclodeca-1, 2, 5, 8-tetraene with mercuric salts in solvents of varying nucleophilicity are described. Instead of forming the usual oxymercuration products reported for reactions of olefins and allenes with mercuric salts, the major products obtained in the present cases result from the initial electrophilic addition of the mercuric salt to the central carbon of the allenic unit forming a mercurinium ion, followed by a transannular attack at the olefinic bonds via a delocalized ion intermediate. Under all conditions, the oxymercuration reaction stereospecifically gives cis-syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol as a predominant product, and the amounts formed are found to be in direct relation to the nucleophilicity of the solvents. A significant amount (54%) of tricyclo[4.4.0.0^{2,4}]deca-5, 8-diene is formed when acetic acid is used as a solvent.

Oxymercuration of Cyclodeca-1, 2, 5, 8-Tetraene

by

Pak-Kong Hong

A THESIS

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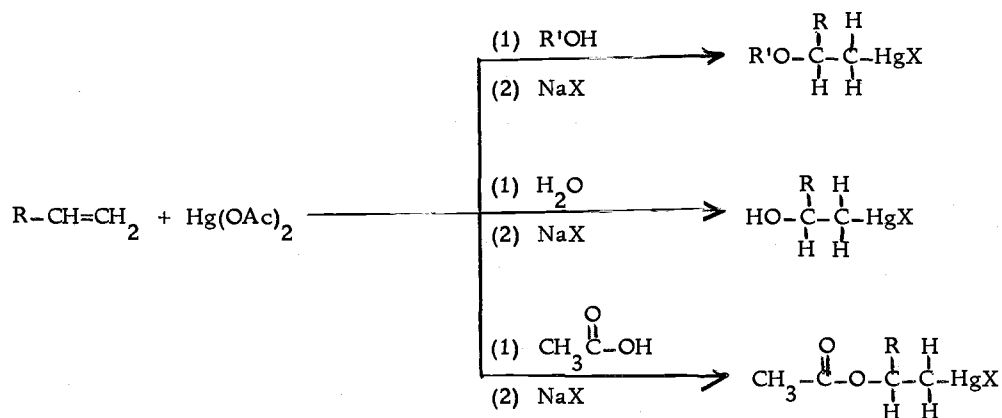
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OXYMERCURATION OF CYCLODECA-1, 2, 5, 8-TETRAENE

INTRODUCTION AND HISTORICAL

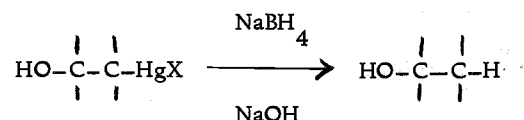
Mercuric salts have been shown to add to olefins in a Markovnikov sense to give 1, 2 addition products. The solvent can also take part in the reaction and the products are usually isolated as the halomercurial by treatment with aqueous sodium halides because the halogen derivatives usually will precipitate out of the reaction mixture for easier isolation and purification.



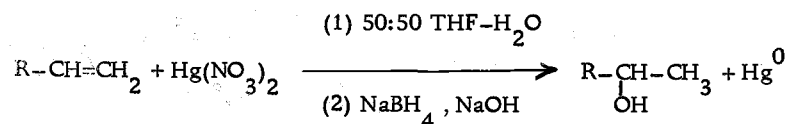
Oxymercuration has become a reaction of considerable interest and great synthetic utility because it is fast, simple to perform, gives high yields of unrearranged products, and can be applied to various kinds of alkenes (11, 14, 38).

The first successful oxymercuration was developed by Hofmann and Sand in 1900 (27). Since then the reaction has entered a phase of expansion. Sand and Singer (28) first demercurated the mercurial to

the alcohol using sodium amalgam. The reduction of the carbon-mercury bond could be more easily done with sodium borohydride, hydrazine, sodium in liquid ammonia and lithium aluminum hydride (12, 26, 32):



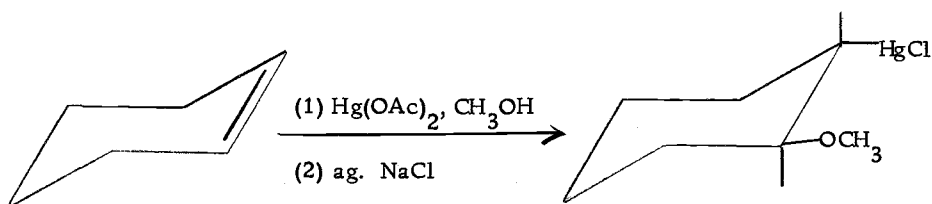
The oxymercuration-demercuration reaction sequence was found to be a very useful tool in the syntheses of alcohols, ethers and esters. Brown (6, 7, 8) and co-workers were very active in this respect, and they described a refined procedure for the syntheses of alcohols from a representative selection of alkenes via oxymercuration of the olefinic compounds with mercuric nitrate in 50:50 mixture of water and tetrahydrofuran, followed by in situ demercuration of the oxymercuration with sodium borohydride in NaOH.



They observed that mono-, di-, tri-, tetraalkyl-, and phenyl-substituted olefins all undergo hydration readily, giving the desired Markovnikov alcohol in high yields (ca. 90%). The solvomercuration-demercuration was most recently extended into a new, convenient route for

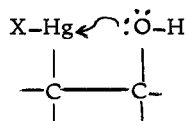
converting olefins into the Markovnikov esters, ethers (10), amides (9), amines (9, 24), alkyl peroxides (4), and azides (18).

Oxymercuration of acyclic and monocyclic olefins occurs in a stereospecifically trans fashion. Numerous investigations have established this beyond question. Among the most important ones, Brook and Wright (5) used X-ray diffraction to study the oxymercuration product produced by the addition of mercuric acetate to cyclohexene in methanol,



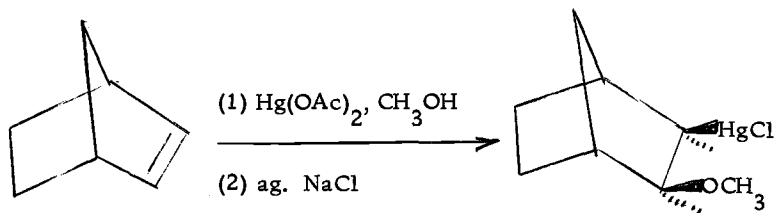
and concluded that the cyclohexane ring was in a chair conformation with methoxy and chloromercuric element occupying vicinal equatorial positions, 4.06 Å apart, trans to each other. This trans configuration was confirmed by nmr studies by Anderson and Henry (1), and Wolf and Campbell (37). Kreevoy and Kowitt (22) found that the oxymercuration product from cyclohexene also eliminates (deoxymercuration) $10^5 - 10^7$ times faster than the cis adduct. This was consistent with tran-addition since the trans isomer would have a much lower enthalpy of activation. Traylor and Baker (32) suggested a method for configurational identification of products from hydroxymercuration of olefins

by studying the displacement of the hydroxyl stretching frequency band into the longer wave region. The cis- β -hydroxy- α -halomercurial products should have a greater displacement, ($18-22\text{ cm}^{-1}$ for cis as compared to $6-10\text{ cm}^{-1}$ for trans) due to the interaction of oxygen with the mercury atom:



In 1969, Waters (34) developed a similar method for establishing the stereochemistry of methoxymercuration by nmr. A greater downfield (deshielding) chemical shift change was found for cis products because the mercury and oxygen was closer.

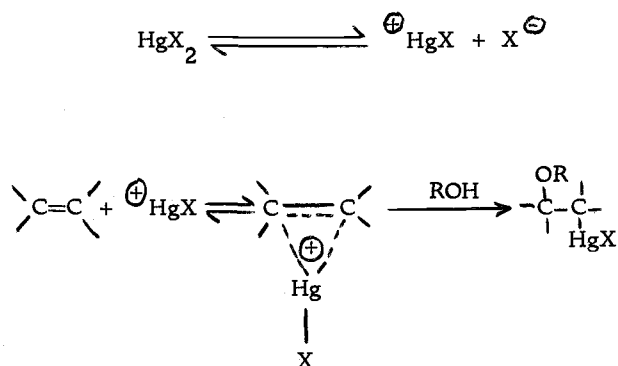
For strained bicyclic olefins, oxymercuration followed a different stereochemical pathway. Norbornene produced stereospecifically exo-cis oxymercurials (31), and no rearrangement accompanied the addition.



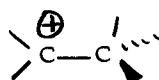
The oxymercuration of bicyclo-[2, 2, 2]-octene might be non-stereospecific depending on the nucleophilicity of the solvent. It gave a mixture of cis and trans products when the reaction was carried out in

aqueous acetone. In glacial acetic acid (low nucleophilicity), the sole product was cis-exo (30).

Ever since Winstein's (23) original proposal in 1939 that oxymercuration of olefins proceeds via a bridged mercury ion intermediate (mercurinium ion), numerous studies have been carried out which have included this species in the mechanistic formulation of their reactions.

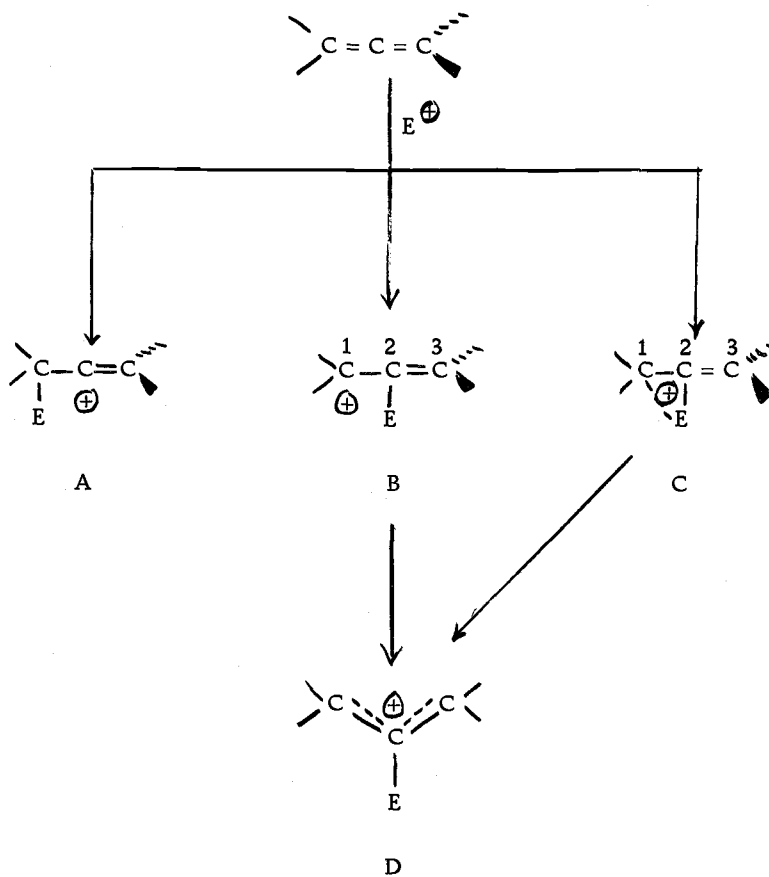


Thus far this mechanism seems to be the most logical one in view of the observed stereochemistry, the kinetics, solvent effects and other evidence of ionic participation (30, 21). One can also preclude that an open carbonium ion (I) may be involved along the reaction pathway, because if this was so, the 1, 2 adduct produced in the oxymercuration could not be completely stereospecific.

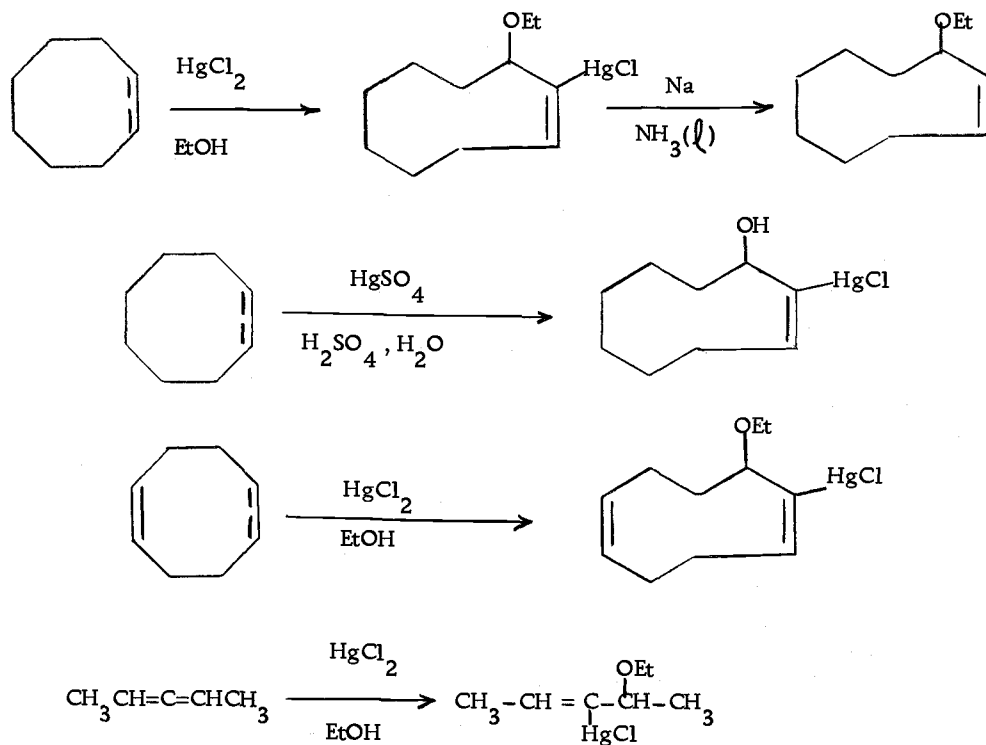


I

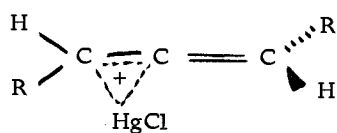
The electrophilic addition of mercuric salts has only recently been extended to allenes. The majority of the mechanistic studies of this reaction have been concerned with the various possible reaction intermediates that can be involved. The addition of an electrophile (E^+ or ^+HgX) to the cumulated orthogonal π -bond system can give rise to either a vinyl cation (A), a non-planar, non-resonated allylic like cation (B), or a bridged ion (C). And, there is a considerable driving force for ions (B) and (C) to go through a 90° bond rotation about c_1 and c_2 to form a planar resonance stabilized allylic carbonium ion (D).



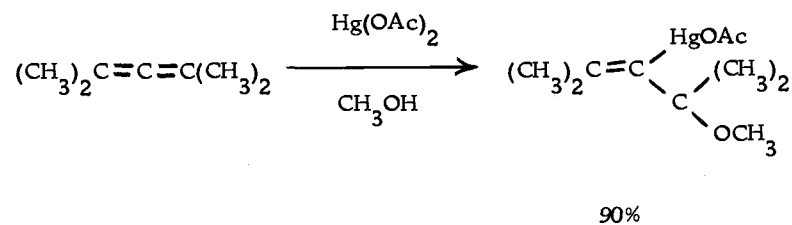
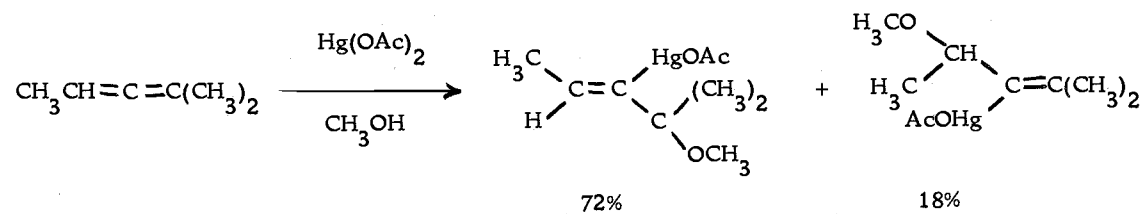
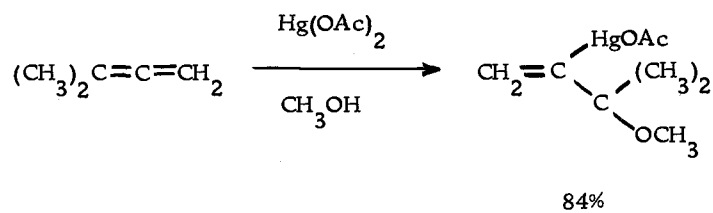
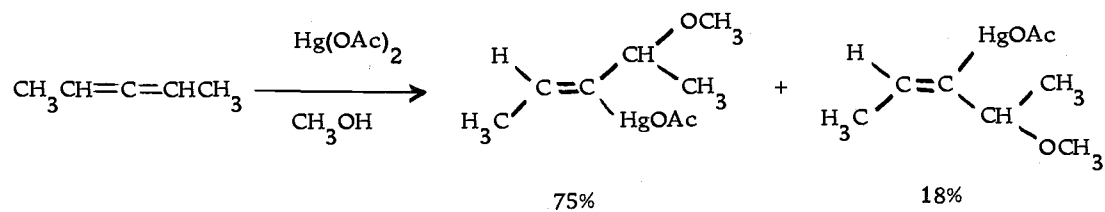
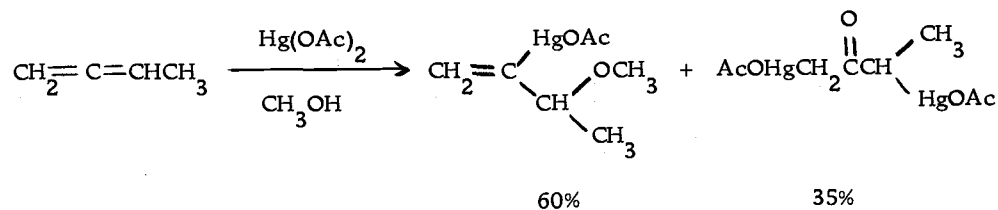
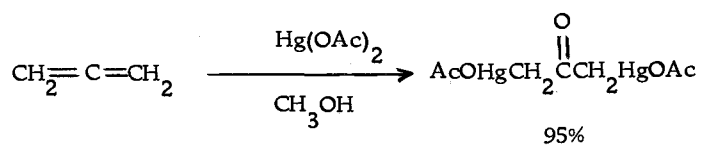
Gardner and co-workers (29) were among the first to report the addition products of mercuric salts to allenes, e. g. 1, 2-cyclononadiene, 1, 2, 6-cyclononatriene, and 2, 3-pentadiene.



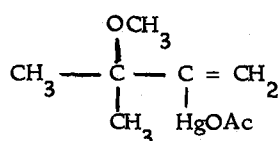
They suggested the reaction intermediate resembled the bridged ion (C).



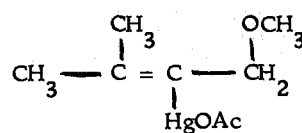
Soon after this, Waters and Kiefer (35) expanded this subject by a thorough study of methoxymercuration on a complete series of methyl substituted allenes.



From the above results, they presented their generalization that the methyl substituents lead the initial attack of the electrophile to the center carbon atom of the allenic unit, whereas the unsubstituted allenes are attacked at the terminal carbons. They also suggested that the reaction intermediate is a bridged mercurinium ion of type (C), not allylic ion (D). This was best illustrated by the behavior of 1, 1-dimethylallene which gave II, the least stable of the two possible mono-adducts. Attempts to isomerize the monoadduct to the more stable primary ether (III), by heating in solution or treatment with mineral acid were in vain, and the use of bulkier alcohol also failed to change the orientation of the addition.

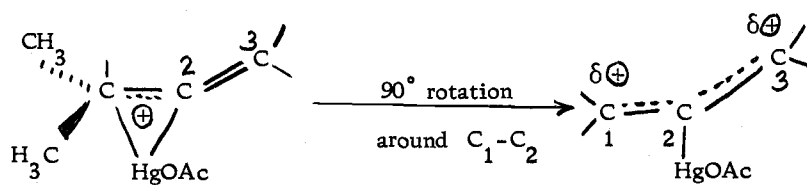


II

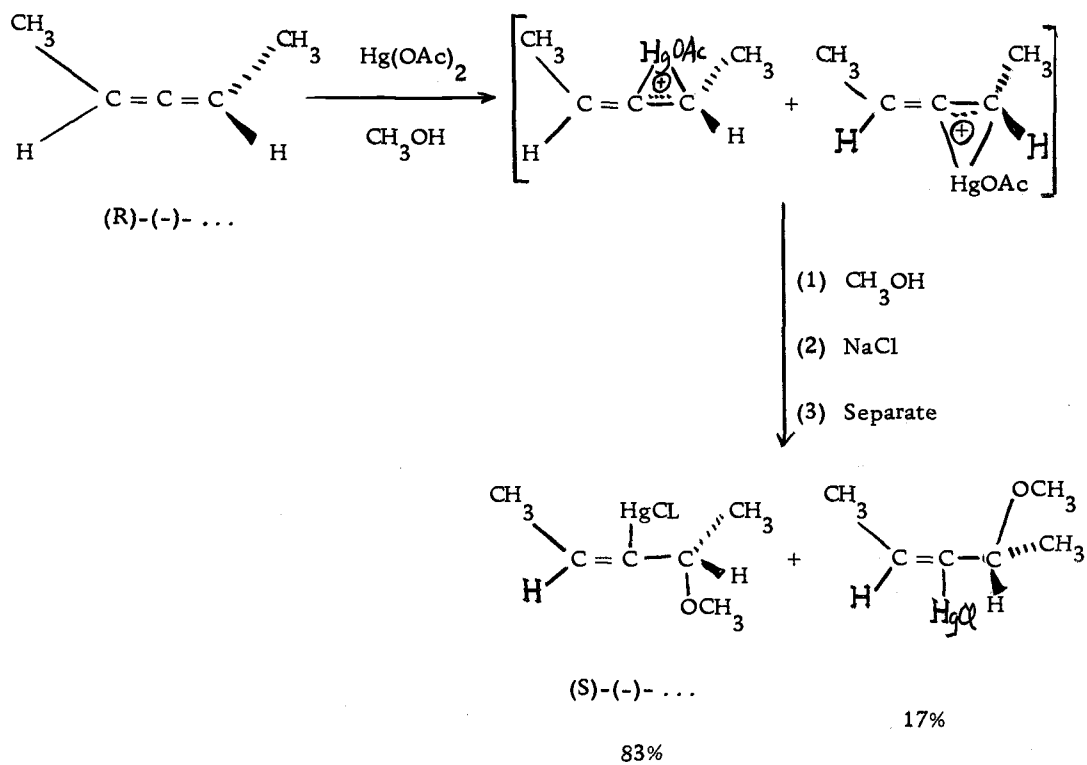


III

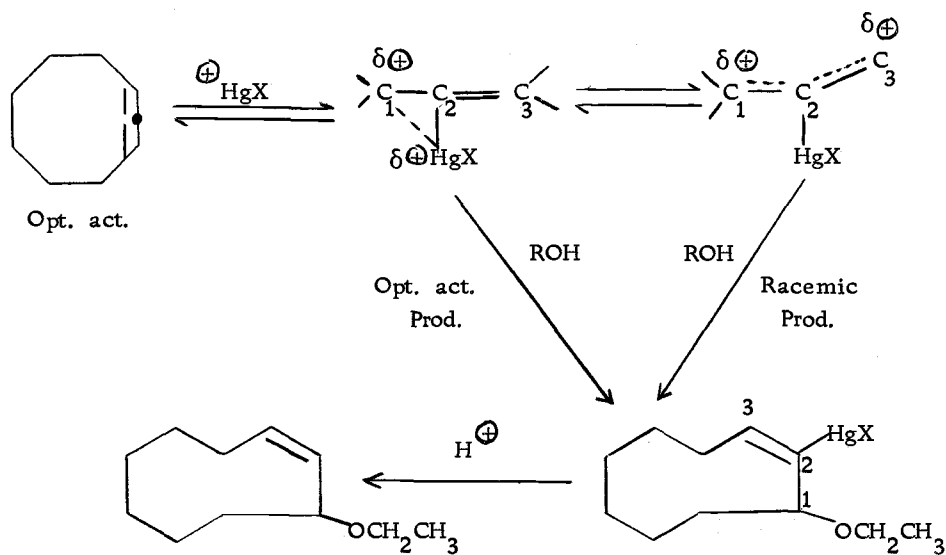
The bonding between the mercury atom and the terminal carbon in the bridged mercurinium ion must be sufficiently strong that it could overcome the resonance energy to be gained by a 90° rotation of the carbon-carbon bond into an allylic carbonium ion.



Further evidence for bridged mercurinium ion was obtained from observation by Waters, Linn and Caserio (36) who showed that the methoxymercuration of optically active (R)-(-)-1, 3-dimethylallene gave rise to optically active trans addition product (S)-(-)-trans 3-chloromercuric-4-methoxy-2-pentane.



Bach's (23) most recent results on the ethoxymercuration of optically active 1,2-cyclononadiene leading to the corresponding optically active cis-3-ethoxynonane also gave convincing evidence for the intermediacy of a mercurinium ion, since the product would be racemic if it had gone through a planar allylic carbonium ion:



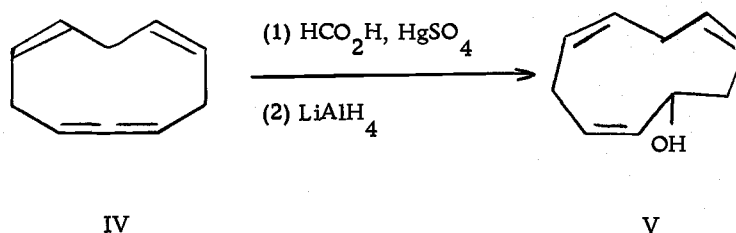
Bach also reported that relative stereospecificity of the reaction is related to the ligand attached to the mercury atom. If a more electro-negative ligand was attached to the mercury atom, it would destabilize the mercurinium ion, enhance the formation of the resonance stabilized allylic carbonium ion, and hence decrease the stereospecificity (Table 1)(3).

Table 1. Reaction of ethanol and optically active, 1, 2-cyclononadiene.

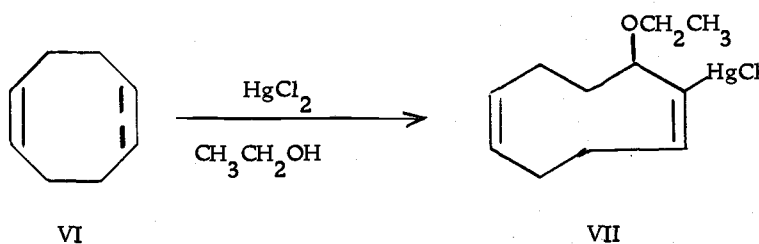
Mercuric Salt	Catalyst	3-ethoxycyclononene	$[\alpha]^{25}_D$, deg
C_2H_5HgOAc	BF_3	85	+15.3
C_6H_5HgOAc	BF_3	42	+13.6
$Hg(OAc)_2$			+12.4
$Hg(OAc)_2$	BF_3	67	+12.6
$Hg(ClO_4)_2 \cdot 9H_2O$	BF_3	82	+12.1
HgO	BF_3	73	+11.1
$HgSO_4$	BF_3	72	+10.4
$Hg(NO_3)_2$		51	+ 9.9
$Hg(NO_3)_2$	BF_3	70	+ 9.9
$HgCl_2Hg(OAc)_2$			+ 6.2
HgF_2	BF_3		+ 1.4
$HgCl_2$			+ 0.1-0.2

RESULTS AND DISCUSSION

When cyclodeca-1, 2, 5, 8-tetraene (IV) is treated with mercuric sulfate in formic acid, the major alcohol product obtained after reduction with lithium aluminum hydride is not the expected cis, cis, cis-2, 5, 8-cyclodecatrienol (V).



This is in contrast to the result reported by Gardner (29), who treated 1, 2, 6-cyclononatriene (VI) with mercuric chloride in ethanol, and obtained the usual oxymercuration product (VII) without rearrangement or transannular reaction.



Allene IV was synthesized by the route given in Figure 1, and subjected to various reaction conditions. The results were as shown in Table 2. The major alcohol product (XI) appeared in all cases, although when acetic acid was used as solvent, approximately half of the product was a hydrocarbon (VIII). Alcohol XI was isolated by gas chromatography

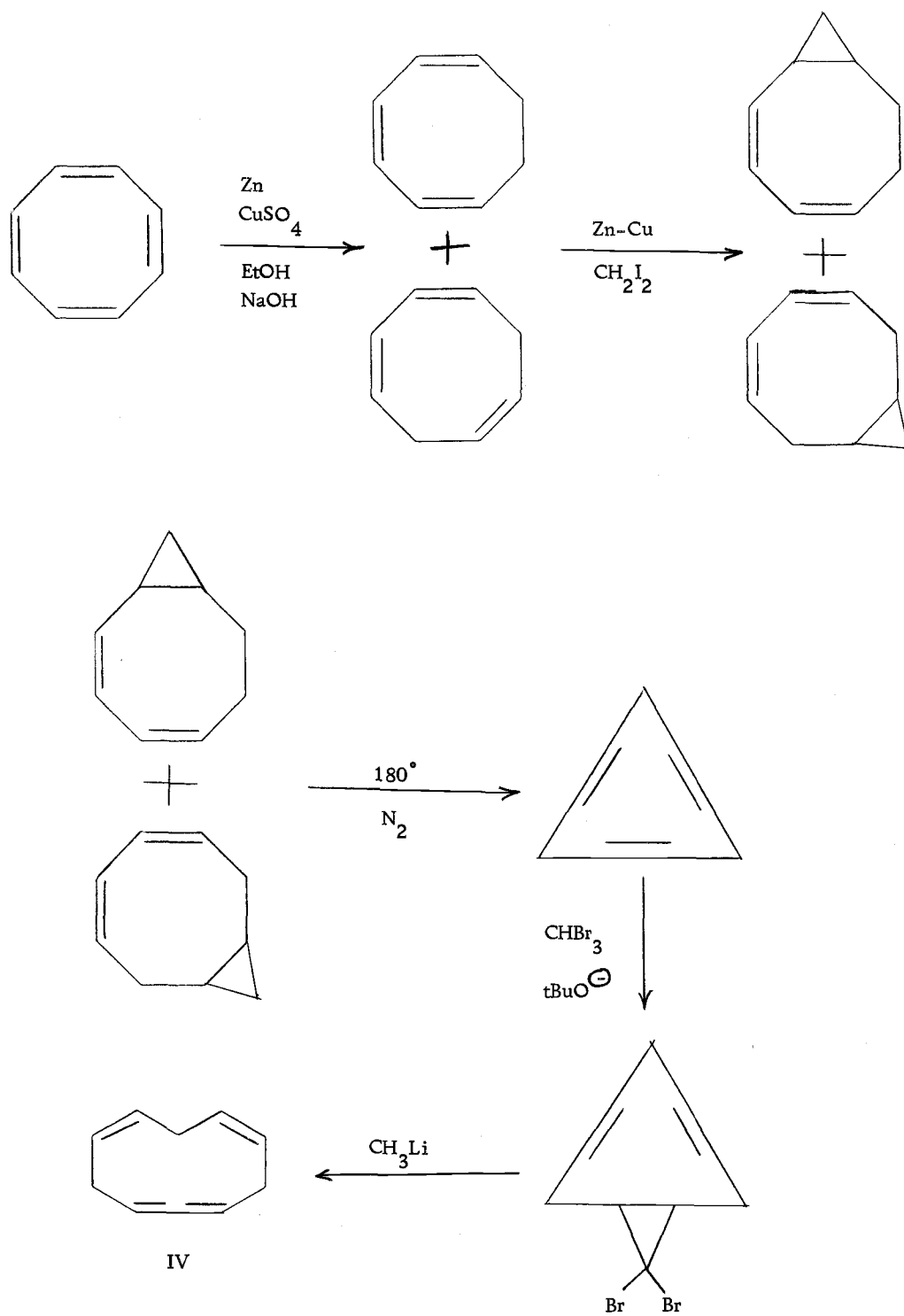
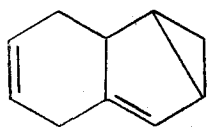


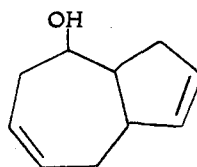
Figure 1. Synthesis of cyclodeca-1,2,5,8-tetraene (IV).

Table 2. Oxymercuration of cyclodeca-1, 2, 5, 8-tetraene (IV).

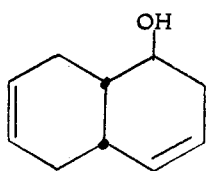
Condition	% Yield	Product Percentage				
		VIII	IX	X	XI	V
(1) HgSO ₄ , HCO ₂ H						
(2) LiAlH ₄	19.1	10.9	13.5	---	63.2	1.5
(1) HCO ₂ H						
(2) LiAlH ₄	23.6	---	11.8	4.3	53.7	14.2
(1) HgSO ₄ , HOAc						
(2) LiAlH ₄	52.1	54.0	2.8	---	43.2	---
(1) Hg(OAc) ₂ , HOAc						
(2) LiAlH ₄	47.2	45.4	4.6	---	50.0	---
HgSO ₄						
60% Aqueous Acetone	67.1	4.6	5.2	---	78.4	11.8



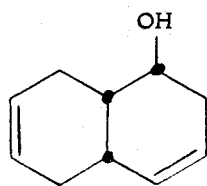
VIII



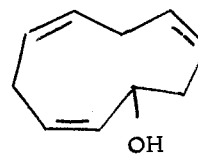
IX



X

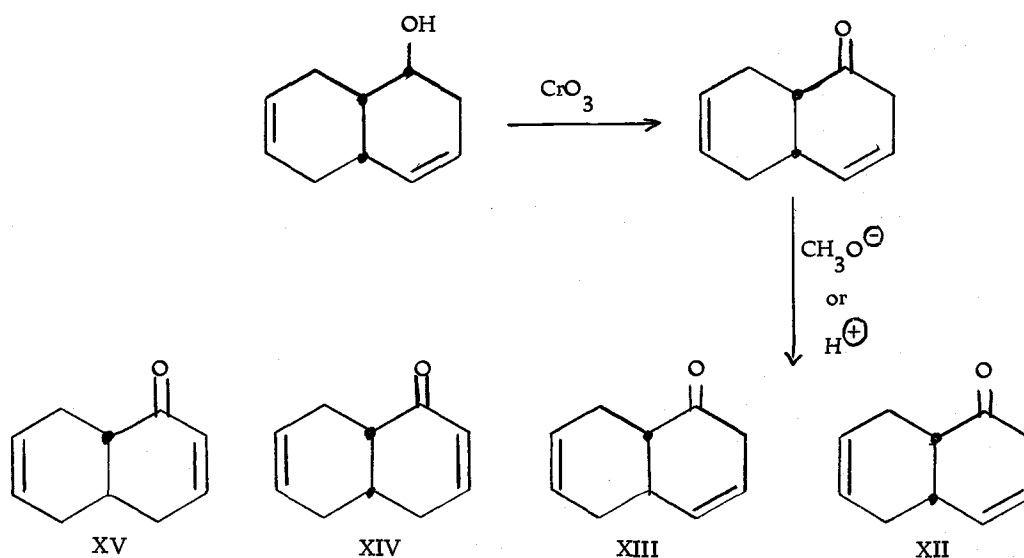


XI



V

It was hydrogenated to a saturated alcohol, with a melting point of 86-89°, and its acid phthalate derivative melts at 169-170°. These agreed closely with the literature values for cis, syn-1-decalol and its acid phthalate derivative (m p. 93° and 176° respectively)(13). The infrared spectrum of the saturated alcohol was identical to that of the authentic cis, syn-1-decalol. Alcohol XI was also oxidized to the corresponding ketone which showed only end absorption in ultraviolet and an IR_{max} at 1720 cm⁻¹. This was presumably the β,γ-unsaturated ketone (XII), which was isomerized in either base or acid to give three new compounds. From infrared and ultraviolet spectra, the one close to XII on gas chromatography was identified as the trans fused β, γ-unsaturated ketone (XIII), the other two, with longer retention times, were the α, β-unsaturated ketones, (XIV) and (XV).



The nmr spectrum of XI (Figure 2) exhibited signals for the hydroxyl proton at δ 1.1 (s, 1), the allylic and homoallylic protons centered at

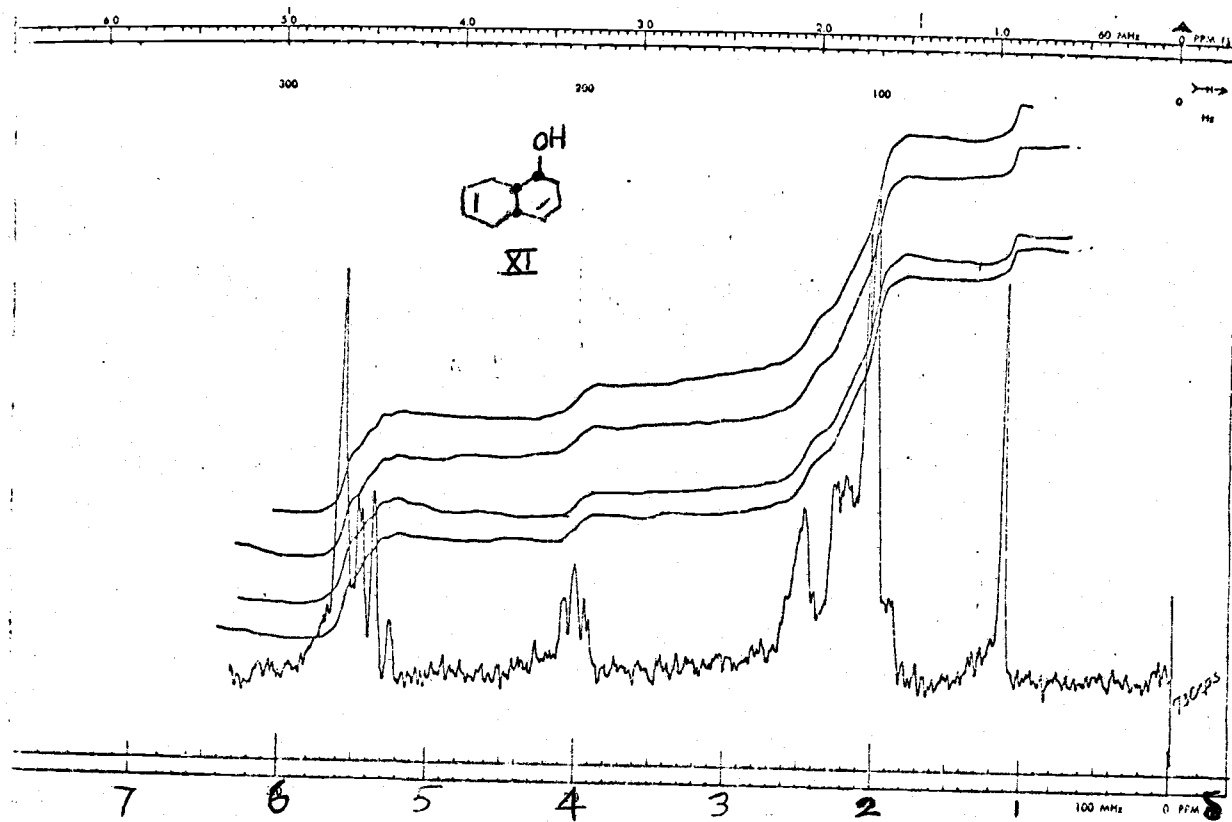
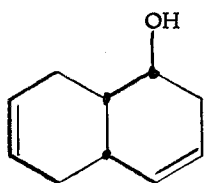
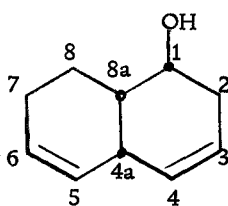


Figure 2. NMR spectrum of cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol (XI).

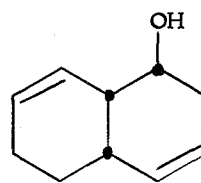
δ 2.1-2.5 (m, 8), the proton on the carbon bearing the hydroxy group at δ 4 (q, 1), and the vinyl protons at δ 5.2-5.7 (m, 4). All the above spectral and chemical evidence plus the C and H analysis led to the conclusion that alcohol XI must be cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol, although the nmr spectrum could also fit the isomeric alcohols XIA, or XIB, when only considering the number of vinyl protons, the proton at δ 4, and the hydroxyl proton.



XI



XI A



XI B

Structure XIA and XIB were ruled out because XIA would have two homoallylic protons at C₈ which usually absorb at about δ 1.6-1.7, more upfield than the one shown in Figure 2, and XIB would also have signals at around δ 1.7-1.8 for the doubly homoallylic protons at C₅.

The mechanism for the formation of alcohol XI is proposed in Figure 3. Since all the oxymercuration reactions studied here stereospecifically gave the cis-syn isomer (XI), the intermediate must involve a delocalized ion (XVI), so that the solvent could only attack the back side to give the desired products. If an open carbonium ion

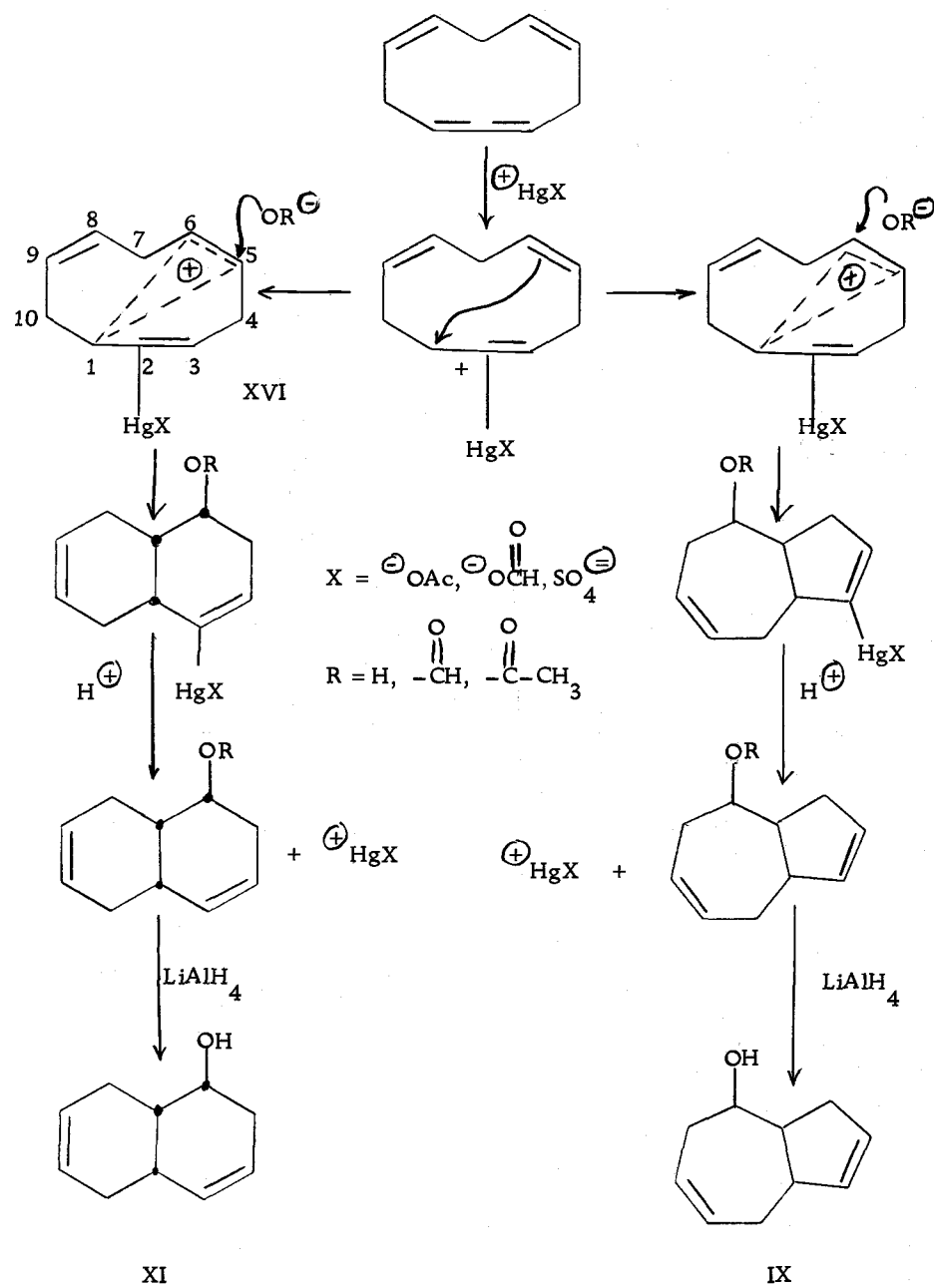
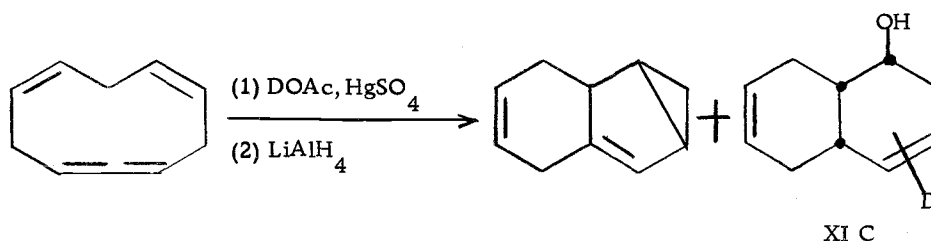


Figure 3. Mechanism for the formation of alcohols XI and IX.

was formed at C₅, there would be some cis-anti isomers X formed. When deuterated acetic acid was used instead of glacial acetic acid, deuterium was found to have incorporated into the alcohol (XIC) as shown by mass spectrum (Table 3) and nmr spectrum (3 vinyl protons, instead of four). This is consistent with the proposed demercuration step in the mechanism.



Two attempts were made to synthesize alcohol XI by a different route, but both were unsuccessful. The sequence shown in Figure 4 was carried out. After the second Birch reduction with lithium and liquid ammonia, a complex mixture of products resulted, and no desired ether could be isolated. The second synthesis attempt was a combination of Diels-Alder and Chugaev reactions (Figure 5). The preparation of the Δ^6 -cis-Octalin-1,4-diol gave no problem, but the subsequent xanthate preparation and pyrolysis was unsuccessful. The pot material showed unreacted diol and perhaps some xanthate, but definitely no alcohol XI was formed.

The major hydrocarbon product isolated when acetic acid was used as solvent can best be represented as VIII. The mass spectrum

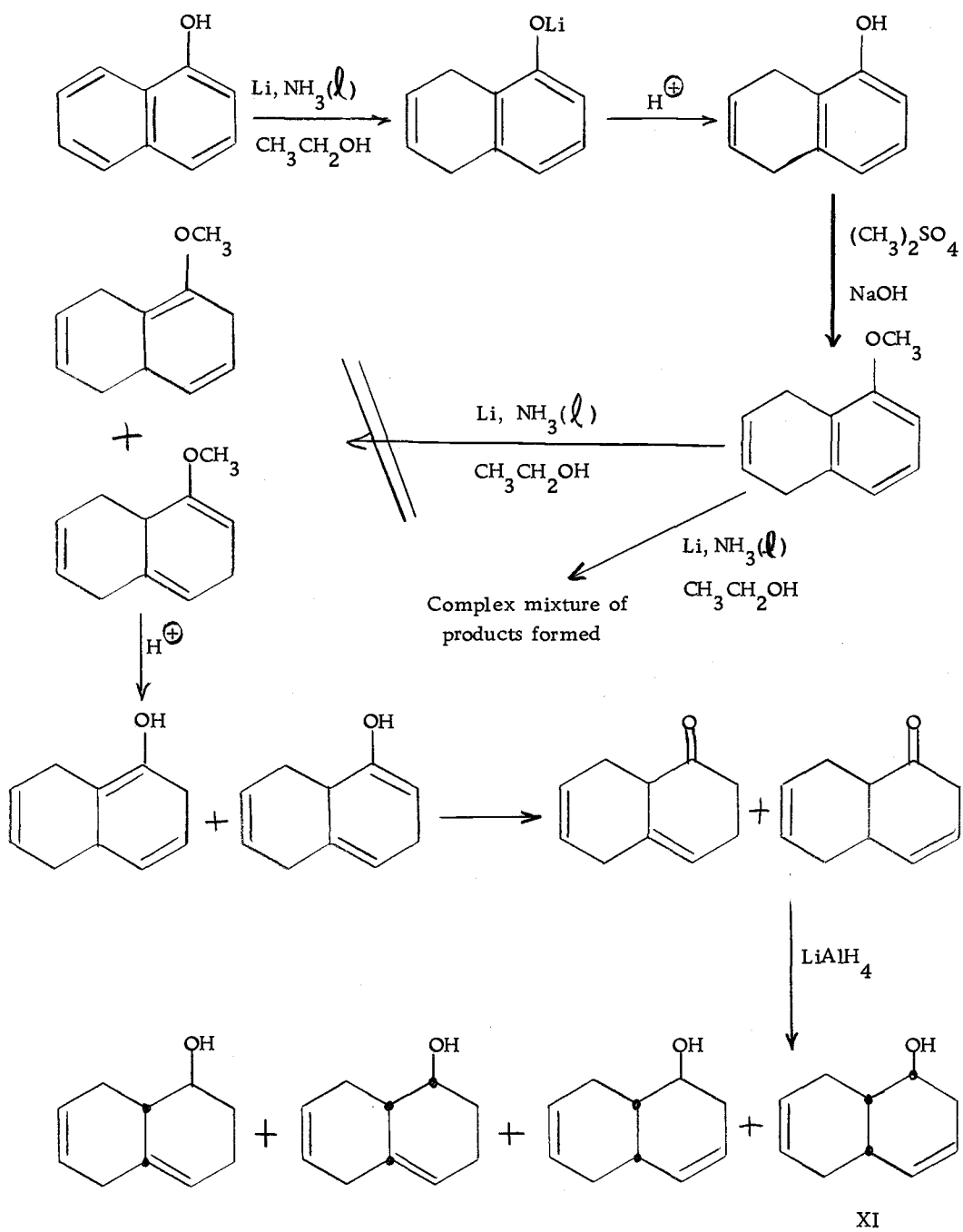


Figure 4. First attempted synthesis of alcohol XI.

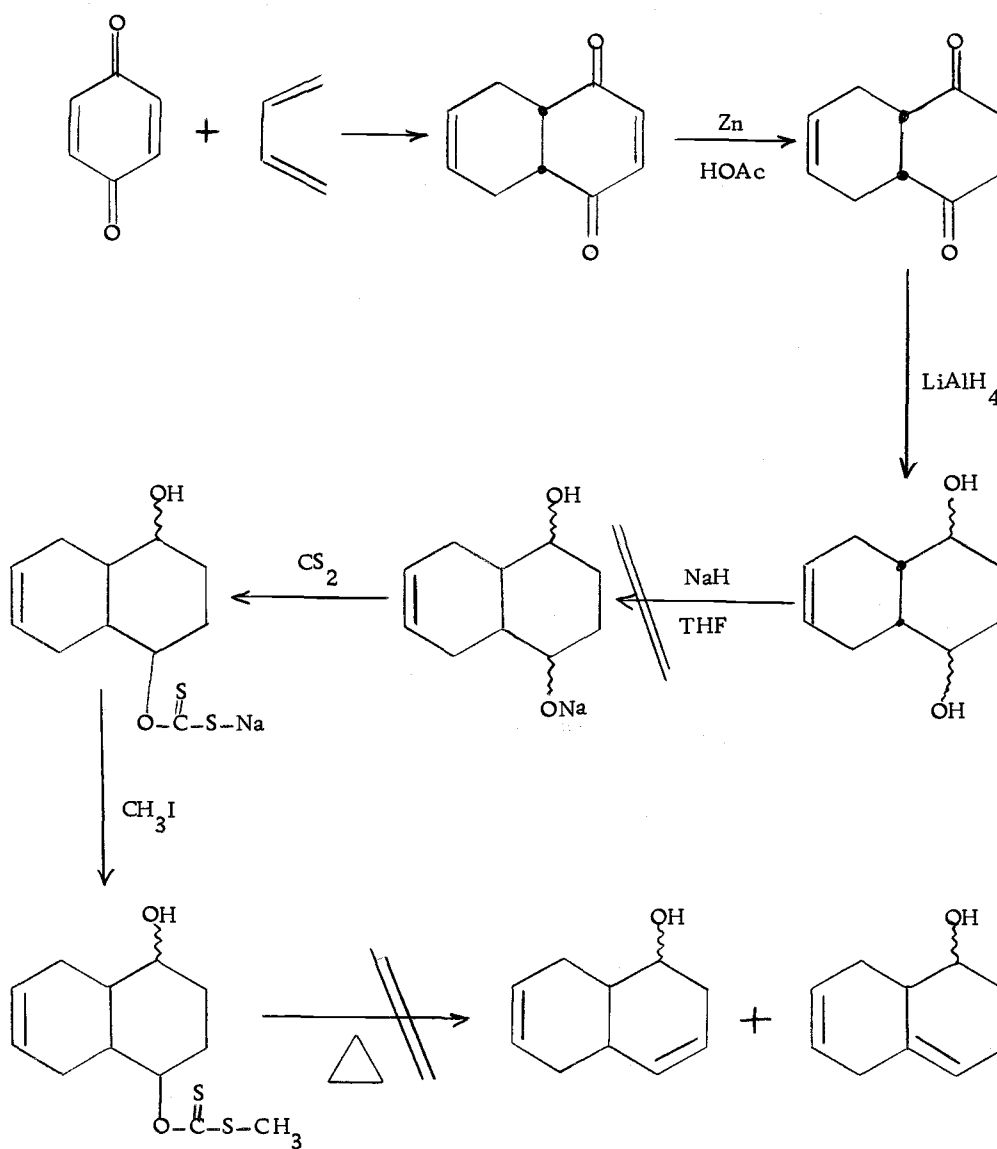
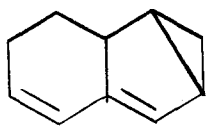
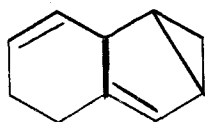


Figure 5. Second attempted synthesis of alcohol XI.

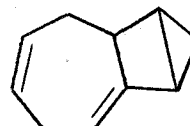
gave a mass peak at 132 and the C and H analysis agreed with the proposed structure. The ultraviolet spectrum showed only end absorption. Upon hydrogenation, the hydrocarbon (VIII) gave both cis and trans decalin which were confirmed by gas chromatography retention times and direct mass spectra comparison. Its nmr spectrum (Figure 6a) showed the cyclopropyl protons upfield at δ 0 (m, 1), and δ 0.4-0.7 (m, 1), the vinyl protons at δ 5.3-5.7 (m, 3), and the remaining methylene and methyne protons at δ 1.3-3.1 (m, 7). Although this spectrum of the hydrocarbon could also fit structures VIIIA, VIIIB, and VIIC, the ultraviolet spectra eliminates structure VIIIA and the hydrogenation data eliminate structure VIIC. Structure VIII B is not ruled out but



VII A



VII B



VII C

is mechanistically difficult to explain. The nmr spectra of Bicyclo [3, 1, 0] hex-2-ene, (17), closely resembles that of VIII (Figure 6b). A possible mechanism for the formation of VIII is given in Figure 7. It was not certain how the HgX^{\oplus} comes off in the last step. Two postulations are shown. It might go through a concerted pathway, or a metal complex of a carbenoid intermediate as recently suggested by Gassmann and co-workers (16). They would both give the desired product.

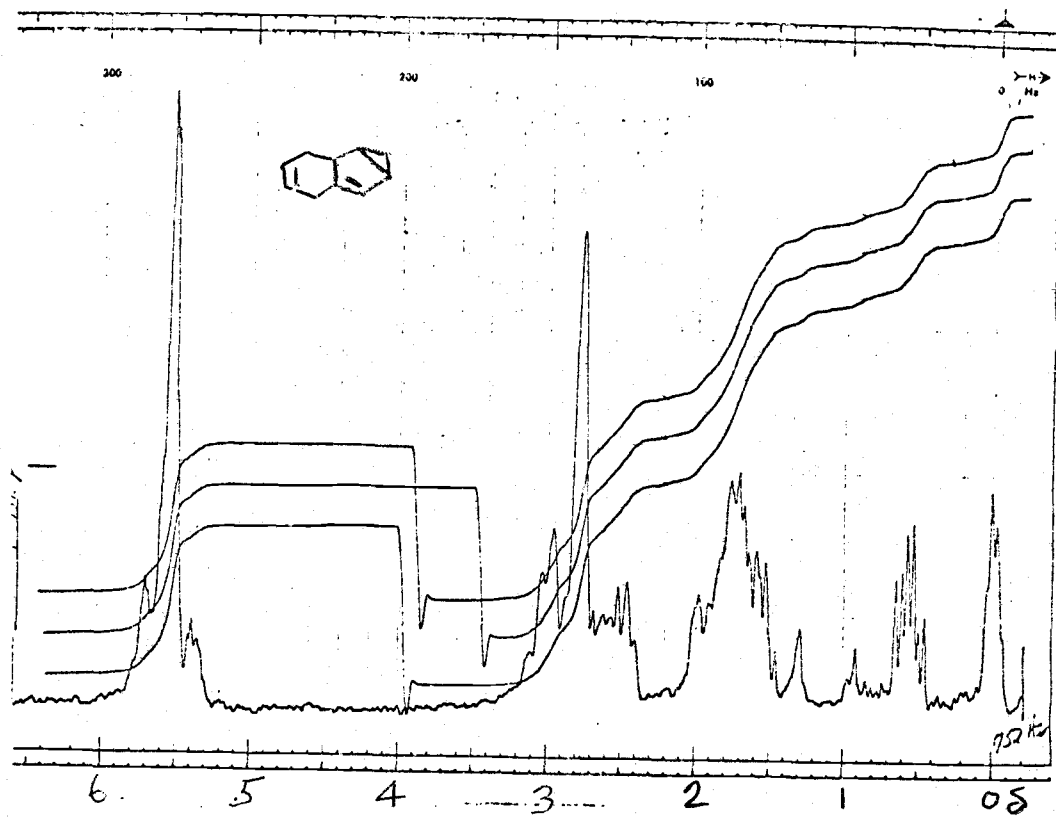


Figure 6a. NMR spectrum of tricyclo[4.4.0.0^{2,4}]deca-5,8-diene.

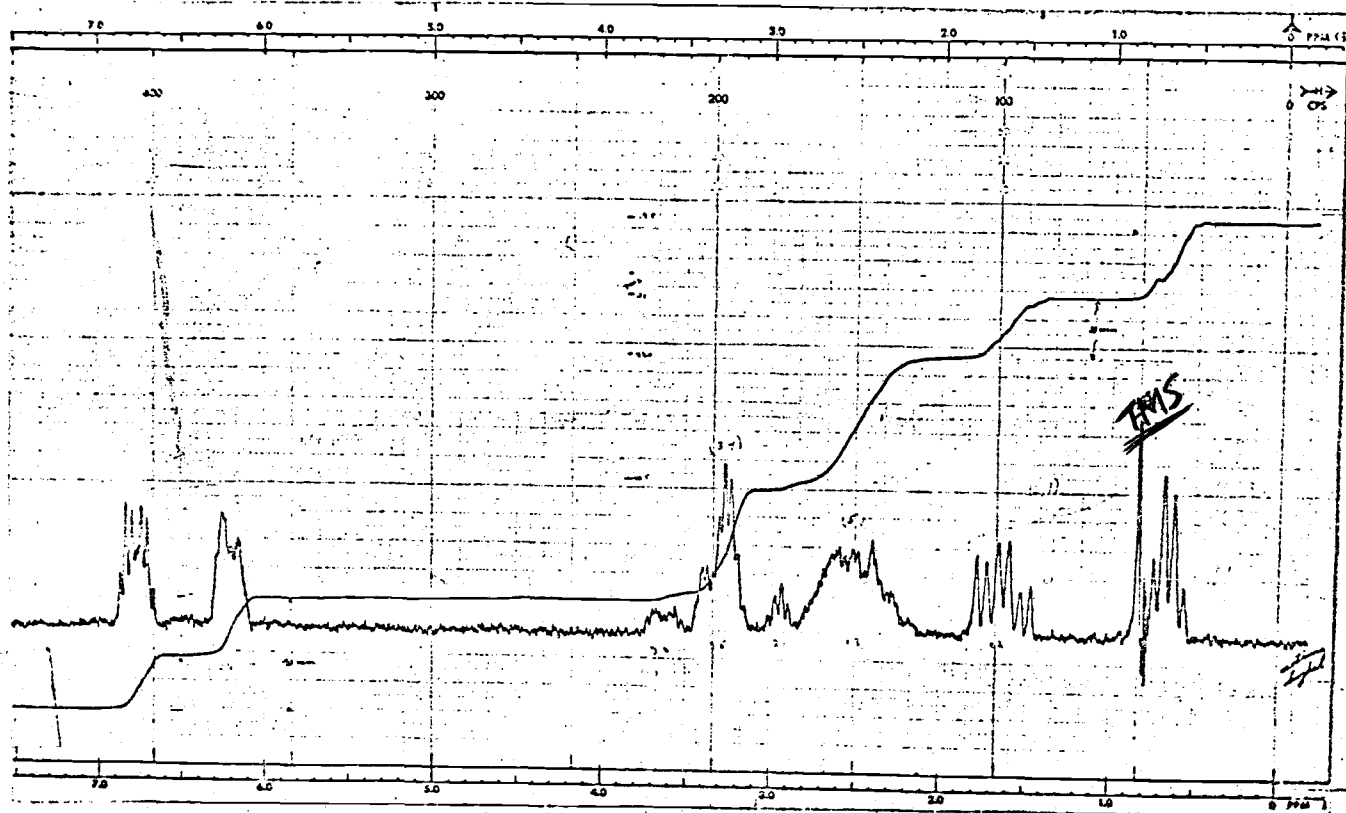


Figure 6b. NMR spectrum of bicyclo[3.1.0]hexene-2 in CDCl_3 .

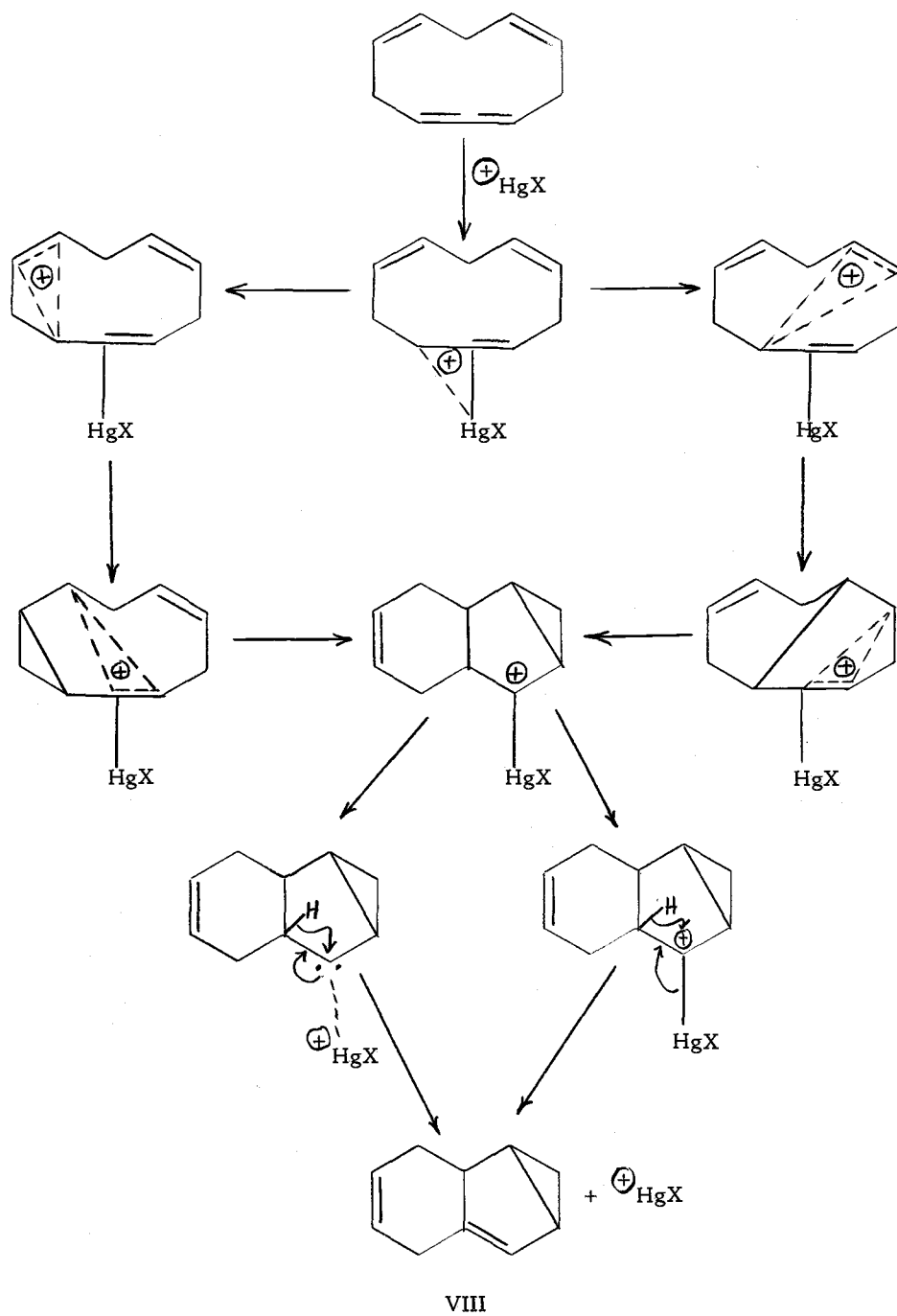
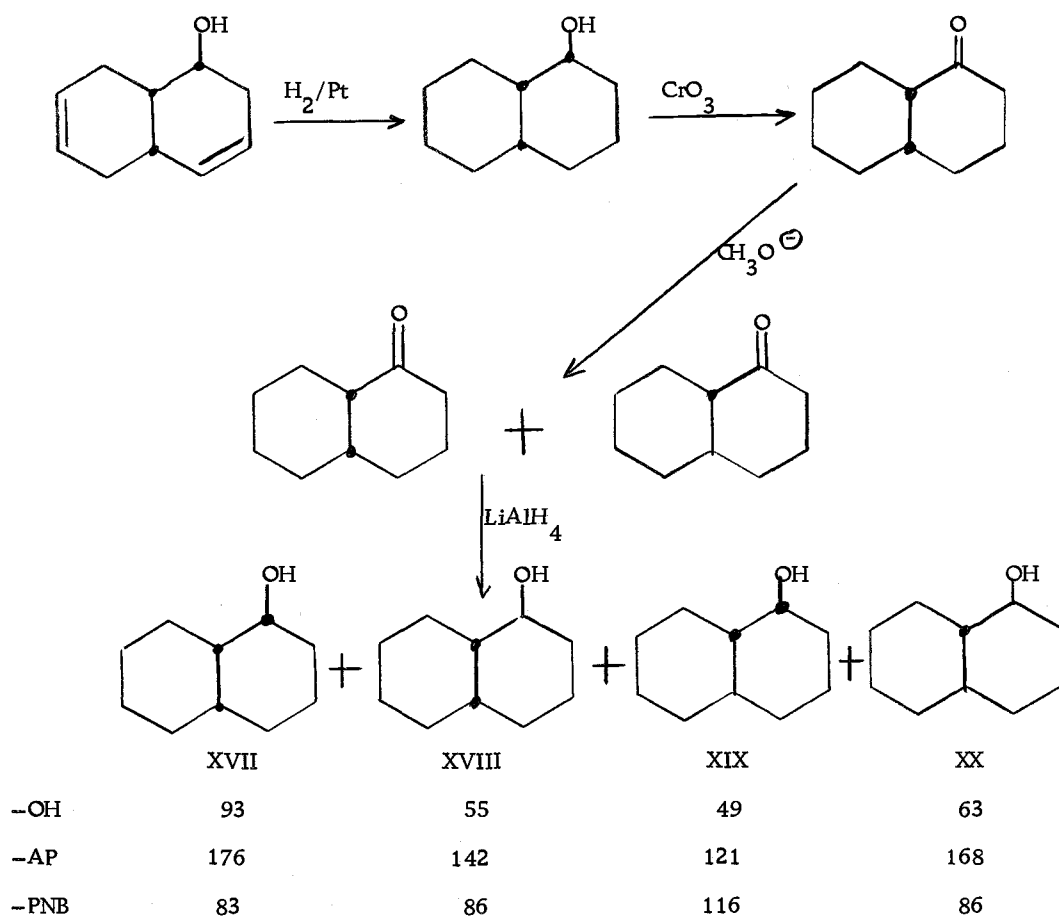
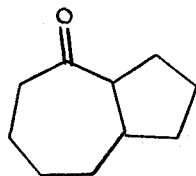


Figure 7. Mechanism of the formation of hydrocarbon VIII.

Very small amounts of alcohol IX were obtained. It was first believed to be the trans fused isomer of either X or XI. Accordingly, alcohol XI was hydrogenated, oxidized to the corresponding ketone, isomerized in base, and reduced with lithium aluminum hydride to give four saturated alcohols: XVII, XVIII, XIX and XX. The melting points of the alcohols and their acid phthalate and p-nitrobenzoate derivatives were reported by Dauben (13).



When alcohol IX was hydrogenated and co-injected into the mixture of the above four saturated alcohols, its retention time was found to be different from all of them. This suggested that IX might be a seven-five member ring fused alcohol which could also be explained by the same mechanism as for alcohol XI (Figure 3). Subsequently, alcohol IX was hydrogenated and oxidized to the corresponding ketone (XXI), which was found to have identical mass spectrum (Table 2) as the



XXI

authentic sample of XXI. Thus one could conclude that the structure of alcohol IX was as proposed. The stereochemistry of IX was not studied, but it was most likely the cis-syn isomer.

Alcohol X was identified by retention time on gas chromatography alone. It was co-injected with the mixture of alcohols obtained by reducing ketone XII with lithium aluminum hydride, and was found to have the same retention time as the cis-anti isomer. Alcohol V was also identified on basis of retention time by co-injection with the authentic sample.

The amount of alcohol XI formed was found to be in direct relation to the nucleophilicity of the solvents: aqueous acetone > acetic

acid > formic acid. Significant amounts of hydrocarbon VIII were obtained only when acetic acid was used. It was found to be very stable in acetic acid but unstable in formic acid (refer to Experimental). In the case of aqueous actone, the transannular delocalized ion intermediate (Figure 3) must have been mostly captured by the more nucleophilic solvent water to form alcohol XI before it had a chance to rearrange to form the hydrocarbon (VIII).

EXPERIMENTAL

All melting points were determined by the Cole-Parmer melting point apparatus and are uncorrected. The infrared spectra were run on a Beckman I. R. 8 Infrared Spectrophotometer. All the ultraviolet spectra were recorded with a Cary Model 15 Recording Spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Model HA-100 Analytical NMR Spectrometer. The mass spectral data were obtained with the Atlas CH7 Mass Spectrometer with glc inlet. All elemental analysis were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, West Germany.

Cycloocta-1, 3, 5-triene and Cycloocta-1, 4, 6-triene

A mixture of 780 ml of ethanol (95%), 405 g of zinc dust, and 90 ml of water was added to a three-liter three-necked round bottom flask equipped with a good reflux condenser. This was mechanically stirred and refluxed while a solution of 1.3 g of cupric sulfate in 9 ml of water was then added, followed by the addition of 370 g of cyclooctatetraene. The oil bath was removed and the flask was placed into an ice bath. From a dropping funnel, 63 ml of 40% (by weight) sodium hydroxide was added dropwise over a 20 minute period, cooling as necessary to maintain a steady reflux. Near the end of the addition the refluxing stopped and the oil bath was used again to maintain a

gentle reflux for another three hours. The reaction mixture was filtered through celite and the solid was washed twice with 500 ml of pentane. The liquid was mixed with 2.4 liters of water. The organic layer was separated and the water layer was extracted twice with 400 ml of pentane. The yellow pentane layers were combined and washed twice with one liter of water and were dried over magnesium sulfate. After removing the magnesium sulfate and solvent, the product was distilled under reduced pressure (80-85°, at 21 mm), yielding 333 g of triene, a mixture of isomers (90% yield). The nmr spectrum showed signals centered at δ 5.5 (m, 6) and at δ 2.5 (m, 4).

Preparation of Zn-Cu Couple

A solution of 5.7 g of cupric acetate in 570 ml of glacial acetic acid was brought to boiling in a one liter flask and 350 g of 20 mesh granular zinc was added. The flask was swirled for three minutes and the solution was suction filtered. The Zn-Cu couple was washed with 570 ml of boiling glacial acetic acid and 2.5 lbs of anhydrous ether. The Zn-Cu couple, 359 g, was stored in a desiccator.

Bicyclo[6. 1. 0]nona-1, 2-diene and Bicyclo[6, 1.0]nona-2, 4-diene

A mixture of 280 g of cyclooctatriene (Mixture of isomers), 260 g of Zn-Cu couple, 790 ml of anhydrous ether and a few crystals of iodine was mechanically stirred in a three-liter three-necked flask

equipped with a very good reflux condenser. The mixture was brought to reflux with an infrared lamp, then 835 g of methylene iodide was added dropwise over one hour. After about 2.5 hours the reaction refluxed on its own without heating, and some cooling was required later. The infrared lamp was used again, after the reaction stopped refluxing, to maintain a gentle refluxing for five more hours. The mixture was cooled in ice and quenched with 650 ml of saturated ammonium chloride, and filtered through Celite. The ether layer was separated and washed with saturated ammonium chloride (2 x 500 ml, 1 x 250 ml), 5% sodium bicarbonate (2 x 150 ml), saturated sodium chloride (1 x 250 ml), and dried over anhydrous magnesium sulfate. The ether was distilled off and the product was vacuum distilled at 1 mm and oil bath temperature at about 80°. This gave 224 g of product, containing some starting triene, the nmr spectrum showed, signals at δ 0.7-0.9 (m, 2), at δ 1.7-2.6 (m, 6) and at δ 5.1-5.9 (m, 8).

Cis, cis, cis-1, 4, 7-cyclononatriene

One fourth of the above product, 56 g, was pyrolyzed in a sealed ampule for six hours at 180°. The resulting mixture was cooled and poured into an ice-cooled mixture of 150 g of silver nitrate, 150 ml of water and 100 ml of 95% ethanol and stirred for two hours. The solid silver complex was collected on a Buchner Funnel and washed three times with 60 ml portions of 2:1 ethanol-water, twice with 100 ml

of ethanol and, finally, five times with 50 ml portions of pentane. Each washing was done by transferring the solid into a large beaker, stirring the solid and the washing liquid thoroughly, and collecting the solid again. The silver complex was then added to a solution of 250 ml of concentrated ammonium hydroxide and 125 ml of water and extracted twice with 250 ml portions of pentane. The pentane extracts were washed with water, saturated sodium chloride solution, and dried over magnesium sulfate. After distilling off the pentane, 6.5 g of 1,4,7-cyclononatriene were recovered. Melting point 47-48°C.

Cis, cis, cis-10, 10-Bicyclo[7, 1, 0]deca-3, 6-dienyl dibromide

A solution of 10 g (0.09 mole) of cis, cis, cis-1,4,7-cyclononatriene in 35 ml of pentane in a 250 ml three-necked flask was stirred with a mechanical stirrer and chilled in an ice-salt bath, while 10 g of potassium tertiary butoxide was added under nitrogen (solution turns amber color), followed by 6.6 ml of bromoform which was added dropwise over 4.5 hours. (5 ml of pentane was added after the addition of 3.5 ml of bromoform because the mixture was too thick for efficient stirring). At the end of the bromoform addition, 10 ml of water and 10 ml of pentane were added and the brown solid was filtered off. The filtrate was washed three times with water and once with saturated salt solution. After drying over sodium sulfate, the solvent was distilled off. The crude brownish solid was distilled under vacuum at oil

bath temperature 80-90°, yielding 6.5 g of the desired mono-adduct. The bis-adduct remained undistilled. The pure mono-adduct melts at 57.5-58.5°. The nmr spectrum showed a complex pattern at δ 5.5-6.2 (m, 4) and δ 2.9-3.6 (m, 1), δ 2.0-2.7 (m, 5), and δ 1.8-2.1 (m, 2). The infrared spectrum showed peaks at 3010 cm^{-1} (vinyl C-H), 710 cm^{-1} (cis double bond).

<u>Analysis:</u>	Calculated:	% C	41.11	% H	4.14
	Found:	% C	41.13	% H	4.19

Cyclodeca-1, 2, 5, 8-tetraene (IV)

A solution of 3 g of the above dibromide in 8 ml of ether was stirred and chilled in dry ice-acetone and 8 ml of 1.75 M methyl lithium was added over 30 minutes under nitrogen. The temperature was then raised to -40° for 40 minutes and then two ml of water was added at 0°C. The reaction mixture was washed with water, saturated salt solution until it was neutral to litmus. The ether layer was dried over magnesium sulfate. Removal of the solvent gave 1.8 g of yellowish liquid which was vacuum distilled and 1.1 g of the allene was recovered (78% yield). The infrared spectrum showed a strong band at 1960 cm^{-1} (allene) 3005 cm^{-1} (vinyl C-H), 710 cm^{-1} (cis double bond). The nmr spectrum showed signal at δ 5.2-5.7 (m, 4), δ 4.8-5.2 (m, 2), and δ 2.4-2.8 (m, 6).

<u>Analysis:</u>	Calculated:	% C	90.91	% H	9.09
	Found:	% C	90.76	% H	8.94

Oxymercuration Reactions on Cyclodeca-1, 2, 5, 8-tetraene

a. Mercuric Sulfate and Acetic Acid. A mixture of 65 mg of the allene, 5 mg of mercuric sulfate and one ml of glacial acetic acid was stirred at room temperature for two hours. (The reaction was followed on gas chromatography, and was found to be complete after 30 minutes.) At the end, 15 ml of ether was added, the reaction mixture was filtered to remove unreacted mercuric sulfate. The ether layer was washed twice with water, twice with saturated sodium bicarbonate solution, and dried over magnesium sulfate. (In some cases the hydrocarbon and acetate produced were analyzed before LiAlH_4 reduction.) To the dried ether solution was added 65 mg of lithium aluminum hydride, and stirred for two hours. Then 20% Rochelle salt solution was added to react with the excess lithium aluminum hydride and the ether layer was decanted off, washed with water and dried over magnesium sulfate. After distilling off the solvent, the mixture was chromatographed on 5 ml of Silicar using pentane as eluent. The first 10 ml fraction contained Tricyclo[4,4.0.0^{2,4}]deca-5, 8-diene(VIII). The next two fractions were only pentane. A 20% ether/pentane solution was then used as eluent, and the next four 10 ml fractions contained the alcohol, cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol

(XI), m. p. 83.5-84.5°. The yield of the hydrocarbon was 18.2 mg (28.1%) and that of the alcohol was 16.5 mg (22.5%). This was obtained by comparing peak areas on the gas chromatography with tetralin and 1, 2, 3, 4-tetrahydro-1-naphthol as internal standards. The infrared spectrum of the alcohol showed bands at 3600 cm^{-1} (free OH) $3500\text{--}3200\text{ cm}^{-1}$ (-OH) 3010 (vinyl C-H). The ultraviolet spectrum of the hydrocarbon showed only end absorption. The mass spectrum of the hydrocarbon and the alcohol were given in Table 3. The nmr spectrum of the hydrocarbon was given in Figure 6, and that of the alcohol in Figure 2.

<u>Analysis:</u>	Calculated for VIII:	% C	90.91	% H	9.09
	Found:	% C	90.81	% H	8.94
	Calculated for XI:	% C	79.95	% H	9.39
	Found:	% C	80.18	% H	9.44

b. Mercuric sulfate and Deuterated Acetic Acid. Same procedure as (a) except acetic acid was replaced by deuterated acetic acid. The mass spectrum of the deuterated alcohol was given in Table 3.

c. Mercuric Sulfate, Dioxane. Experiment carried out as (a) replacing acetic acid by Dioxane. (No reaction after 2 hours.)

d. Mercuric Sulfate, Formic Acid. Experiment carried out as (a), replacing acetic acid by Formic acid. The product showed 10.9% of hydrocarbon VIII and 63.2% of alcohol XI.

e. Mercuric Sulfate, Aqueous Acetone. Experiment carried out as (a) replacing acetic acid by 60% aqueous acetone. The product showed 4.6% of hydrocarbon VIII, and 78.4% of alcohol XI.

f. Formic Acid. Experiment carried out as (a) using formic acid alone with no mercuric sulfate. The product showed 53.7% of alcohol XI but no hydrocarbon VIII.

Stability of Products

A small quantity of the acetate from (a) above was stirred in 0.5 ml of acetic acid and mercuric sulfate for 5.5 hours. The reaction was followed by gas chromatography. There was no conversion to the hydrocarbon (VIII). The same stability test was done on hydrocarbon VIII. After four hours no conversion to acetate was observed. Then the hydrocarbon was stirred in formic acid with mercuric sulfate, ca. 80% of the hydrocarbon disappeared, but no formate was observed to form.

Hydrogenation of Tricyclo[4.4.0.0^{2,4}]deca-5,8-diene (VIII)

The hydrocarbon was hydrogenated using the Parr Apparatus at 1.5 atmospheric pressure over night. Platinum oxide was used as catalyst. Two of the products were found to have identical mass spectra as cis and trans decalin. A third product (40%) was not identified.

Hydrogenation of *cis, syn*-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol(XI)

The alcohol was hydrogenated as above giving a saturated alcohol, m. p. 86-89° (*cis, syn*-1-decalol, m. p. 93°) (13). The infrared spectrum of the saturated alcohol was identical to that of authentic *cis, syn*-1-decalol (13). The acid phthalate derivative was prepared by heating 20 mg of the alcohol, 20 mg of phthalic anhydride, and 250 μ l of pyridine at 100° for one hour. The mixture was then poured into 15 ml of benzene, washed with 2 ml of 5% sulfuric acid (twice, cold) and water. After drying over magnesium sulfate the solvent was evaporated giving a solid with melting point 169-170° (literature m. p. 176°)(13).

Cis-2, 5, 8, 4a, 8a-pentahydronaphthalen-1-one (XII)

A portion of *cis, syn*-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol (16 mg) was cooled and stirred in 0.5 ml of acetone. Standard Jones reagent was added until it stayed orange. Ether was added and decanted off. The solid was washed several times with ether and the ether layers were washed with water, saturated sodium bicarbonate and dried over magnesium sulfate. The ketone showed only end absorption in the ultraviolet and an IR_{max} at 1720 cm^{-1} .

Test of Isomerization of *cis*-2, 5, 8, 4a, 8a-pentahydronaphthalen-1-one

The above ketone (XII) was subjected to both acid and base

isomerization:

(a) A sample of the ketone (10 mg) was placed in 0.5 ml of methanol and stirred with five drops of 5% sulfuric acid. After 80 minutes, ten more drops of 5% sulfuric acid were added and stirring continued for another 30 minutes. Ether and water were added, and the ether layer was washed with water, saturated sodium bicarbonate, and saturated sodium chloride and then dried over magnesium sulfate.

(b) Another sample (20 mg) of the ketone was added to an ice-cooled stirred solution of 0.005 g of sodium hydroxide in 0.5 ml of methanol. After three minutes, ether and water were added and the ether layer was washed with water, saturated sodium chloride and dried over magnesium sulfate.

The isomerization products were separated on gas chromatography. There were three new compounds formed in addition to the starting ketone. One of these had retention time very close to XII and showed only end absorption in the ultraviolet and an IR_{max} at 1715 cm^{-1} . The other two showed ultraviolet absorptions at ca. λ_{max} 215 m μ , $\epsilon = 2.5 \times 10^4$ and IR_{max} at about 1680 cm^{-1} , and had much longer retention times, compared to the starting ketone (XXII).

Cis-5, 8, 9, 10-tetrahydro-1, 4-naphthoquinone

The Diels-Alder adduct was prepared by the method described by Fieser and Fieser (15). One third mole (36 g) of pure quinone (The

practical grade quinone was purified by sublimation) was suspended in 500 ml of acetic acid in a one liter flask in an ice bath and 30.5 ml of butadiene, condensed fresh, was added. The flask was closed with a rubber stopper securely wired in place and put in a water bath maintained at a temperature of 15-20°, with occasional swirling to facilitate reaction. At the end of 48 hours, one liter of water and one liter of ether were added. The ether layer was washed with water until neutral and once with sodium bicarbonate solution. After drying over magnesium sulfate, the ether was distilled off. The product recrystallized from benzene-hexane yielding yellow fluffy needles which turned greenish after standing: m. p. 51-53°.

Cis-2, 3, 5, 8, 9, 10-hexahydro-1, 4-naphthoquinone (20)

A portion (10 g) of the above Diels-Alder adduct was dissolved in 25 ml of acetic acid at 50° and poured into a rapid stirring mixture of 13 g of zinc dust in 50 ml of water at 50°. Stirring was continued for 3 minutes and the hot mixture was filtered. Water (150 ml) was added to the filtrate and this was kept at 0° overnight. The white crystals was dried and recrystallized from pet ether to give ca. 7 g of the diketone, m. p. 101-103°.

Reduction of Cis-2, 3, 5, 8, 9, 10-hexahydro-1, 4-naphthoquinone

A mixture of 3 g of the diketone and 2.5 g of lithium aluminum

hydride in 25 ml of ether was stirred overnight. The product showed OH stretching band at ca. 3400 cm^{-1} , and no ketone peak at 1720 cm^{-1} .

Preparation and Pyrolysis of Methyl Xanthate of Δ^6 -cis-octaline-1,4-diol

The xanthate was prepared by the method described in reference (12). To a solution of 1.5 g (0.01 mole) of the diol in 20 ml of dry THF was added 0.23 g (0.01 mole) of metallic sodium. The mixture was refluxed under nitrogen for 44 hours. After removing excess sodium, 0.76 g (0.01 mole) of carbon disulfide was added. The resulting solution was refluxed for 2.5 hours. Methyl iodide (1.42 g, 0.01 mole) was added and the dark brown solution was refluxed for another 3 hours. The solution was cooled and filtered. The inorganic solid was washed with ether and the washing added to the filtrate. Ether and THF are distilled off and the brown solution was distilled at 200° and 0.025 mm. Some yellow liquid was distilled over leaving behind some dark goo in the flask. They were both analyzed on gas chromatography, and showed no peaks corresponding to the desired product. The infrared spectrum showed bands at $3020\text{-}3600\text{ cm}^{-1}$ (OH), 3010 cm^{-1} (C=C), 1050 cm^{-1} (C=S). The xanthate reaction was repeated using sodium hydride instead of sodium. It was also unsuccessful. There was no cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol (XI) isolated.

5, 8-Dihydro-1-Naphthol (25)

A portion of α -naphthol (108 g, 0.75 mole) was added to a three-liter, three-necked flask, equipped with a dry ice condenser, a mechanical stirrer and an inlet tube. The flask was immersed in dry ice. Pure, dry ammonia was charged into the rapidly stirred flask contents and condensed as liquid ammonia by the dry ice condenser until the α -naphthol had gone into solution in about one liter of liquid ammonia. Lithium metal (20.8 g) was added in small pieces at such a rate that the ammonia was not refluxing too violently. The solution was then stirred for 20 minutes, followed by the addition of 170 ml of absolute ethanol which was added dropwise over a period of 30-45 minutes. The condenser was removed. Stirring was continued, and the ammonia was evaporated in a stream of air introduced through the inlet tube. One liter of water was added to the residue, and after the solution was extracted with two 100 ml portions of ether, it was carefully acidified with concentrated hydrochloric acid. The resulting solution was again extracted with three 250 ml portions of ether, and then the ether extract was washed with water and dried over magnesium sulfate. The ether was removed on a rotary evaporator yielding ca. 100 g of crude 5, 8-dihydro-1-naphthol, m. p. 61-65°C. The substance was recrystallized with ether-pentane, and the melting of the purified product was 67-69°.

1-Methoxy-5, 8-dihydronaphthalene (33)

A solution of 6 g of sodium hydroxide in 150 ml of water and also 18 g of pure 5, 8-dihydro-1-naphthol was placed in a 500 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a separatory funnel. The mixture was stirred and cooled to about 10° by immersing the flask in an ice bath. Dimethyl sulfate (12 ml, 16 g) was added dropwise through the dropping funnel during one hour. The reaction mixture was refluxed for two hours and then allowed to cool, added water and transferred to a separatory funnel. It was extracted several times with ether, and the ether extracts were washed with water, dilute sulfuric acid, and again with water until it was neutral to litmus. After drying over magnesium sulfate, the ether was evaporated. The crude product was purified by distillation (82-86°, 0.3 mm), yielding 13 g of the desired methyl ether.

Birch Reduction of 1-Methoxy-5, 8-dihydronaphthalene

A Birch reduction was run on the above methyl ether in the same way for 5, 8-dihydro-1-naphthol, using 13 g of the methyl ether, 300 ml of liquid ammonia, 8 g of lithium, 50 ml of ethanol, and 100 ml of anhydrous ether as solvent. A complex mixture of products was recovered, and nothing pure was isolated.

Table 3. Mass spectra of oxymercuration products.

m/e	Relative Abundance of				
	VIII	IX	XI	XIC	XXI
50	8.1				
51	28.2	3.6	2.3	9.6	3.0
52	12.5	11.8	12.0	47.8	2.4
53	16.7	5.5	6.3	34.8	18.6
54	79.2	15.4	17.1	56.5	22.8
55	6.3	20.9	25.3	58.6	34.3
56		45.5	20.0	41.3	3.9
57		14.5	2.0	7.4	3.3
58	2.9	10.0	11.4	18.7	2.7
59				5.7	
60					
61					
62	2.7				
63	12.3			14.3	
64	9.8	4.6	4.0	9.1	
65	22.9	3.6	2.0	42.1	5.7
66	6.9	18.2	17.1	47.8	8.9
67	5.6	91.0	20.0	69.5	100.0
68		100.0	34.8	36.1	22.9
69		9.1	6.6	11.7	5.7
70		12.7	8.6	12.6	7.1
71		4.6	3.1	6.1	1.9
72		4.6			
73					
74	2.5				
75	3.8				
76	3.5			4.8	
77	26.9			71.6	5.7
78	100.0	25.4	42.8	91.3	2.1
79	22.7	37.2	57.1	100.0	15.7
80	3.8	31.8	70.0	43.5	10.8
81		10.0	22.8	28.7	27.7
82		12.7	28.6	17.0	15.7
83		5.5	4.3	8.3	8.0
84		23.6	10.8		7.9
85		8.2	2.0		2.0
86		4.6	2.0		
87					
88					

Table 3 continued.

m/e	Relative Abundance of				
	VIII	IX	XI	XIC	XXI
89	4.8			6.1	
90	1.7		2.0	3.9	
91	98.0		1.1	91.3	7.1
92	12.5	45.5	100.0	53.5	5.4
93	1.9	8.2	12.0	10.9	16.4
94		6.4	13.7	10.0	5.9
95		6.4	10.8	36.5	43.8
96		22.7	48.6	65.2	7.0
97		14.5	57.1	43.5	6.9
98			5.1		2.3
99					
100					
101					
102	4.7				
103	9.0			8.3	
104	24.6	5.5	5.4	47.8	
105	8.5	22.7	42.8	34.8	2.6
106		10.0	17.1	10.9	3.9
107		6.4	34.1	10.0	1.6
108		4.6	10.8	4.8	16.4
109		2.7	12.6	4.4	10.7
110		4.6	10.0		11.1
111					61.6
112					4.9
113					
114					
115	34.6	8.2	6.0	8.7	
116	18.8	5.5	4.0	10.9	
117	73.0	54.5	40.0	33.4	
118	13.1	7.3	4.8	32.6	
119		4.6	3.4	4.4	4.6
120			1.1		1.7
121			5.4		10.7
122			3.7		4.6
123					
124					
125					
126	14.6				
127	4.8		1.7		

Table 3 continued.

m/e	Relative Abundance of				
	VIII	IX	XI	XIC	XXI
128	10.4	3.6	2.9	4.8	
129	9.4	3.6	2.9	5.2	
130	3.1	2.7	1.4	3.0	
131	16.1	14.5	9.9	11.7	1.4
132	24.0	29.1	62.9	30.0	
133	4.2	4.6	6.3	29.1	
134			3.1	3.9	3.3
135					
136					1.4
137					
138					
139					
140					
141					
142					
143					
144					
145					
146					
147					
148		1.7	1.1		
149		1.9	1.7		
150		4.6	8.6		0.8
151		1.7	1.7		1.5
152					17.1
153					2.5

SUMMARY

The objective of this work was to conduct a mechanistic study of the unusual behavior of cyclodeca-1, 2, 5, 8-tetraene in oxymercuration reactions and try to identify the major products.

Instead of giving the usual oxymercuration products, the allene is apparently first attacked by the mercuric salt at the central carbon of the allenic unit to form a bridged mercurinium ion, followed by a transannular reaction to give a delocalized ion intermediate with the olefinic bond across the ring, and subsequent capture of the solvent or further rearrangement of the delocalized ion would finally give the observed predominant products: an alcohol and a hydrocarbon. The proposed mechanisms for their formation are shown in Figure 3 and Figure 7.

The alcohol was hydrogenated to give cis, syn-1-decalol, oxidized to yield a β , γ -unsaturated ketone, and the mass spectrum, C and H analysis, and nmr spectrum all led to the conclusion that the alcohol be cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol (XI). Two alternative routes were tried to synthesize the alcohol, but failed. The hydrocarbon contained no conjugated double bonds because its ultraviolet spectrum showed only end absorption. It was hydrogenated to give cis and trans decalin. Its nmr spectrum had upfield cyclopropyl protons and three vinyl protons. With additional information

from mass spectra and C and H analysis, the hydrocarbon was best represented as tricyclo[4.4.0.0^{2,4}]deca-5,8-diene (VIII).

The other minor products from the oxymercuration reactions were identified by comparing either their retention times on gas chromatography or their mass spectra with some authentic compounds.

BIBLIOGRAPHY

1. Anderson, M. M. and P. M. Henry. N. M. R. Spectra and conformation of Hg(II) addition products of cyclohexene and 2-norbornene. *Chemistry and Industry*, no. 50, p. 2053-2054. 1961.
2. Bach, R. D. The addition of water and alcohols to allenes catalyzed by mercuric salts. *Tetrahedron Letters*, no. 56, p. 5841-5844. 1968.
3. Bach, R. D. The stereospecificity of the alkoxymercuration of allenes. *Journal of the American Chemical Society* 91:1771-1777. 1969.
4. Ballard, D. H., A. J. Boodworth and R. J. Bunce. The alkyl peroxymercuration of terminal alkenes: a synthesis of secondary alkyl peroxides and β -functionally substituted peroxides. *Journal of the Chemical Society (D)*, 1969, p. 815-816.
5. Brook, A. and G. Wright. The configuration of the diastereomeric 1-chloromercuric-2-methoxycyclohexanes. *Acta Crystallographia* 4:50-58. 1951.
6. Brown, H. C. and P. J. Geoghegan. Solvomercuration-demercuration. I. The oxymercuration-demercuration of representative olefins in an aqueous system. A convenient mild procedure for the Markovnikov hydration of the carbon-carbon double bond. *Journal of Organic Chemistry* 35:1844-1850. 1970.
7. Brown, H. C. and W. J. Hammar. Stereoselectivity of the hydration of representative cyclic and bicyclic olefins of the new oxymercuration-demercuration procedure. *Journal of the American Chemical Society* 89:1524-1525. 1967.
8. Brown, H. C., J. H. Kawakami and S. Ikegami. A remarkable stereoselectivity in the oxymercuration-demercuration of norbornene, 7,7-dimethylnorbornene and related derivatives. *Journal of the American Chemical Society* 89:1525-1526. 1967.
9. Brown, H. C. and J. T. Kurek. The solvomercuration-demercuration of representative olefins in the presence of acetonitrile. A convenient procedure for the synthesis of amines. *Journal of the American Chemical Society* 91:5647-5648. 1969.

10. Brown, H. C. and M. H. Rei. The solvomercuration-demercuration of representative olefins in the presence of alcohols. Convenient procedures for the synthesis of ethers. *Journal of the American Chemical Society* 91:5646-5647. 1969.
11. Chatt, J. The addition compounds of olefins with mercuric salts. *Chemical Review* 48:7-44. 1951.
12. Cope, A. C. (editor-in-chief). *The Organic Reactions*. Vol. 12. New York, John Wiley and Sons, Inc., 1962. 538 p.
13. Dauben, W. G., R. C. Tweit and C. Mannerskantz. Decahydronaphthoic acids and their relationship to the decalols and decalylamines. A stereochemical study of the reaction of nitrous acid with decalylamines. *Journal of the American Chemical Society* 76:4420-4426. 1954.
14. Eliel, E. L. and N. L. Allinger (editors). *Topics in stereochemistry*. Vol. 3, New York, Interscience Publishers, 1968. 377 p.
15. Fieser, L. and M. Fieser. *Basic Organic Chemistry*. Boston, D. C. Heath and Company, 1959. 369 p.
16. Gassmann, P. G., T. I. Atkins and F. J. Williams. The effect of alkyl substitution on the course of the rearrangements of derivatives of bicyclo[1, 1, 0]butane promoted by metal carbonyls. *Journal of the American Chemical Society* 93:1812-1813. 1971.
17. Grostic, M. F. Electrophilic and free radical additions to bicyclo[3, 1, 0]hexene-2. Ph. D. Thesis. Moscow, University of Idaho, 1964. 164 numbered leaves.
18. Heathcock, C. H. New synthesis of alkyl azides. *Angewandte Chemie* 8:134-135. 1969.
19. Henbest, H. B. and B. Nicholls. Aspects of stereochemistry. Part XII. A specific directing effect in the mercuration of some 4-substituted cyclohexanes and cis-hex-3-enol. *Journal of Chemical Society*, 1959, p. 227-236.
20. Henbest, H. B., M. Smith and A. Thomas. Aspects of stereochemistry. Part X. The preparation and hydration of ditertiary vicinal epoxide of the decalin series. *Journal of Chemical Society*, 1958, p. 3293-3298.

21. Kitching, William. Some aspects of oxymetalation. *Organometallic Chemistry Reviews* 3:61-133. 1968.
22. Kreavoy, M. M. and F. R. Kowitt. The nature of the rate-determining step in deoxymercuration. *Journal of the American Chemical Society* 82:739-745. 1960.
23. Lucas, H. J., F. R. Hepner and S. Winstein. The coordination complex of mercuric ion with cyclohexene. *Journal of the American Chemical Society* 61:3102-3106. 1939.
24. Perie, J. J. and A. Lattes. Reaction D'Aminomercuration III Nouvelle Methode D'Obtention D'Aminomercuriques Par Desoxyaminomercuration. *Tetrahedron Letters*, no. 27, p. 2280-2292. 1969.
25. Rabjohn, N. (editor-in-chief). *Organic synthesis. Collective Vol. IV.* New York, John Wiley and Sons, Inc., 1963. 1036 p.
26. Robson, J. H. and F. F. Wright. The autoxidation of organomercuric salts. *Canadian Journal of Chemistry* 38:21-23. 1968.
27. Sand, J. and K. A. Hofmann. Uber das Verhalten von Mercurisalzzen gegen olefine. *Chemische Berichte* 33:1340-1352. 1900.
28. Sand, J. and F. Singer. Mercruis-Verbindungen aus Terpinel und Dimethylheptenol. *Chemische Berichte* 35:3170-3187. 1902.
29. Sharma, R. K., B. A. Soulders and P. D. Gardner. Oxymercuration of allenes. *Journal of Organic Chemistry* 32:241-244. 1967.
30. Traylor, T. G. Oxymercuration of olefins. II. cis- and trans-oxymercuration of bicyclo[2, 2, 2]oct-2-ene. *Journal of the American Chemical Society* 86:244-248. 1964.
31. Traylor, T. C. and A. W. Baker. Cis Oxymercuration of Norbornene. *Tetrahedron Letters*, no. 19, p. 14-18. 1959.
32. Traylor, T. G. and A. W. Baker. The oxymercuration of olefins. I. A general method for determination of the stereochemistry of oxymercuration. *Journal of the American Chemical Society* 85:2746-2752. 1963.

33. Vogel, A. I. A text-book of practical organic chemistry including qualitative organic analysis. 3rd edition. New York, John Wiley and Sons, Inc., 1966. 1188 p.
34. Waters, W. L. The stereochemistry of methoxymercuration. I. A facile method of configuration assignment by N. M. R. Spectroscopy. Tetrahedron Letters, no. 43, p. 3769-3772. 1969.
35. Waters, W. L. and E. F. Kiefer. Methoxymercuration of allenes. Evidence of a σ -bridged mercurinium ion. Journal of the American Chemical Society 89:6261-6268. 1967.
36. Waters, W. L., W. S. Linn and M. C. Caserio. The stereochemistry of addition reactions of olefins. I. Methoxymercuration and halogenation of 1, 3-dimethylallene. Journal of the American Chemical Society 90:6741-6749. 1968.
37. Wolfe, S. and P. G. Campbell. Cyclohexen-3, 3, 6, 6-d₄. A useful compound for the study of mechanism and structure. Canadian Journal of Chemistry 43:1184-1198. 1965.
38. Zefirov, N. S. Stereochemistry of the hydroxymercuration of alkenes. Russian Chemical Review 34:527-536. 1965.

APPENDIX

APPENDIX

Nuclear Magnetic Resonance Spectrum of Cis, syn-
1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol with
Added Shift Reagent

Some new structural information of alcohol XI has been obtained when its nmr spectrum was run with added shift reagent, $\text{Eu}(\text{fod})_3$. As the amount of $\text{Eu}(\text{fod})_3$ was increased, the signals shifted downfield, and the spectrum was greatly clarified and simplified. The nmr spectrum of alcohol XI is as shown in Figure 8 when 100 mg of shift reagent was added. The shift effects were greater on protons closer to the hydroxy group. (The hydroxyl proton and the proton on C_1 , H_1 , are off scale.) Protons on C_2 are moved farthest downfield to δ 9.2-9.4 (H_2), and δ 10.9 (H_2). When H_1 was irradiated, H_2 and H_2 , sharpened up to doublets, and H_{8a} changed to a sharper singlet. When H_2 was irradiated, H_2 collapsed to a broad singlet. When H_2 was irradiated, H_2 collapsed to a doublet with a small coupling constant, and H_3 sharpened up to a doublet. Proton H_{8a} changed to a sharper singlet and H_7 became a clear doublet when H_8 was irradiated. As H_8 was irradiated, H_8 collapsed to a singlet. These decoupling experiments confirmed the positions of the double bonds at C_6 - C_7 and C_3 - C_4 . All the other protons are designated as shown in Figure 8. Protons H_{4a} , H_5 and H_5 , did not move too much since they are so far away from the hydroxy group.

The above pronounced shift effects observed for protons H_2 , $H_{2'}$, H_{8a} , H_8 and $H_{8'}$, and the results from decoupling experiments have provided conclusive evidence that alcohol XI is cis, syn-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol.

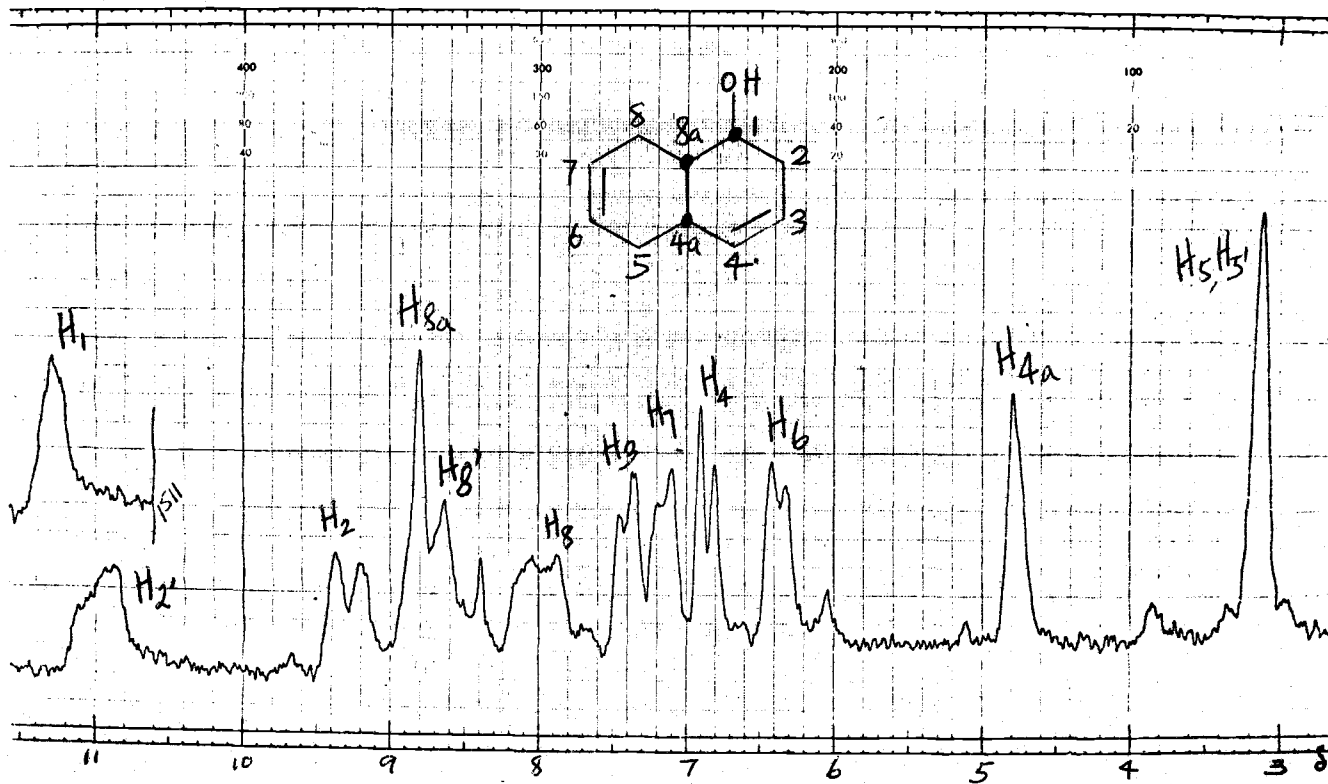


Figure 8. NMR spectrum of *cis, syn*-1, 2, 5, 8, 4a, 8a-hexahydronaphthalen-1-ol with added shift reagent, $\text{Eu}(\text{fod})_3$.