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Thermal and photochemical rearrangements of bicyclic epoxides and ketones

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THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF BICYCLIC EPOXIDES AND KETONES

by

David Lawrence Garin

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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Approved:

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

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VITA

The author was born in New York City on June 14, 1939. He attended Boys High School in New York and was graduated in June, 1955. In September of 1955, he enrolled at The Bernard Baruch School of Business Administration, a branch of The City College of New York. In March of 1957, dissatisfied with the field of accounting, he dropped out of college. In September of 1957, he resumed his education at The City College majoring in chemical engineering. In September, 1958, his interest in chemistry resulted in his switching to that major field. In June, 1960, he received his Bachelor of Science degree from The City College. The author was awarded a National Science Foundation summer research fellowship from The City College where he worked under Dr. H. Salzburg during the summer of 1960.

In September of 1960, the author began his graduate studies at Iowa State University as a teaching assistant in organic chemistry under Dr. O. L. Chapman. After one year, he was given a research assistantship. The author completed the requirements for his degree by August, 1964, with a major in organic chemistry and minors in biochemistry and physical chemistry. In November, 1964, he was granted the degree, Doctor of Philosophy, from Iowa State University.

INTRODUCTION

It has been known for many years that heat or Lewis acids can cause epoxides to rearrange (1, 2, 3, 4). The mechanism is not known, but products can often be predicted by analogy making the rearrangement a useful tool in synthesis.

In the past few years, the photochemical transformation of conjugated dienes has made it possible to explore strained bicyclic olefins (5). Two such compounds are bicyclo(3.2.0)-hept-6-ene and bicyclo(4.2.0)oct-7-ene. The corresponding epoxides appeared to be interesting compounds due to the excessive strain of the fused rings and the fact that they were substituted cyclobutene oxides, a class of compounds that had not been studied previously.

This exploration resulted in expansion to:

a. The pyrolysis of cyclobutene oxides and norbornene oxide.

b. The Lewis acid-catalyzed rearrangement of cyclobutene oxides.

c. The rearrangement of cyclobutene oxides with lithium aluminum hydride.

d. The pyrolysis of cyclobutanones and norbornanone (norcamphor).

e. The photolysis of cyclobutanones and norbornanone.

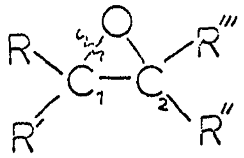
HISTORICAL

In discussing the rearrangements of the bicyclic epoxides, it is well to review the rearrangements of epoxides in general and then go on to the specific case of the cyclobutene oxides. The unique nature of the corresponding ketones does not necessitate a discussion of photolysis and pyrolysis of ketones in general. Instead, discussion is limited to the photolysis of cyclic and bicyclic ketones and the pyrolysis of cyclobutanones.

Since this research was begun, other investigators have reported experiments that have a direct bearing on this work. These experiments will be dealt with in the Results and Discussion section as examples and analogies to this research.

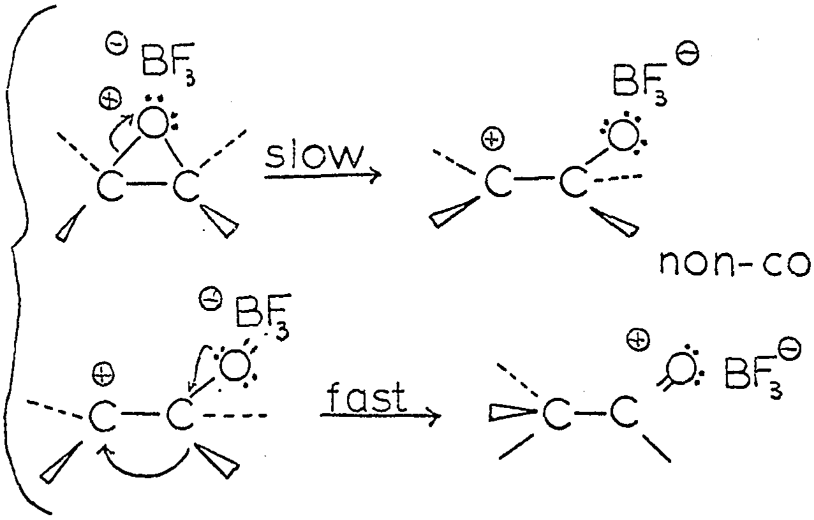
The Rearrangement of Epoxides

Heat or Lewis acids can cause an epoxide to rearrange to an aldehyde or ketone (1, 2, 3, 4). The course of the rearrangement process is governed by two factors: the direction of ring opening and the relative migratory aptitude of the different substituent groups. The direction of the ring opening is determined by the ease of breaking of the carbon-oxygen bond, as shown by the effect of electron-releasing groups, which always facilitate breaking of the bond between oxygen and the carbon atom to which they are attached. This substituent effect of electron releasing groups (groups which



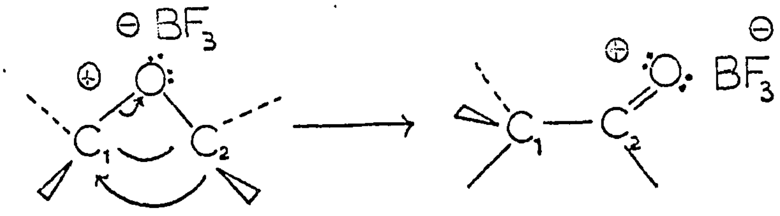
R, R' more electron-releasing than R'', R''' thus C_1-O bond cleaves

(A)



non-concerted

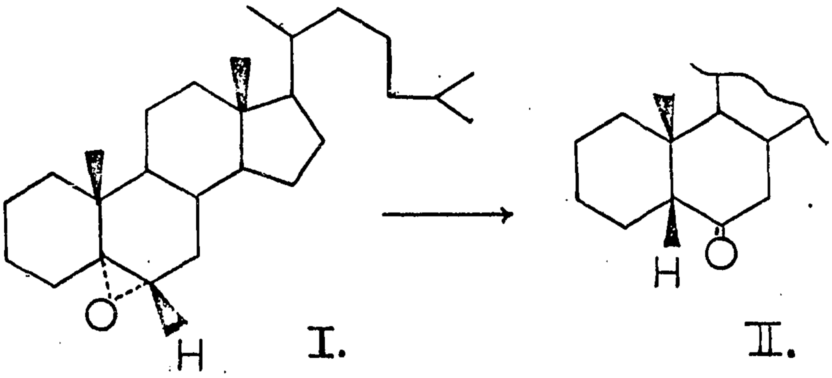
(B)



concerted
with inversion
at C_1

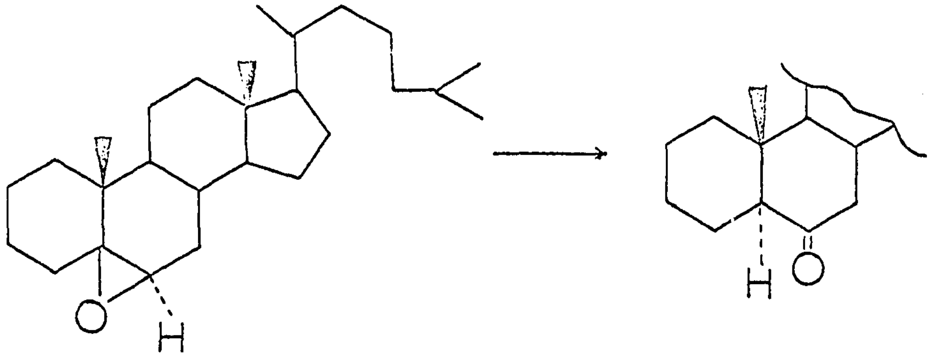
stabilize an adjacent positive charge) must mean that the reaction is either a two-stage process involving a rate-determining unimolecular breakage of the oxide ring, followed by a migration step (equation A), or a one-stage concerted process (but still unimolecular) in which carbon-oxygen bond breaking is more important in the transition state than is bond making (equation B) (1). When these reactions are catalyzed by Lewis acids, the entity which rearranges is presumably the acid-epoxide complex, as depicted in equations A and B.

If the epoxide-to-carbonyl conversions follow the concerted path, they should undergo inversion at the migration terminus (C_1) in the process (6). Two well defined examples are the boron trifluoride-catalyzed isomerizations of 5α, 6α-epoxycholestane (I) to coprostan-6-one (II) and 5β, 6β-epoxycoprostane (III) to cholestan-6-one (IV) (7).



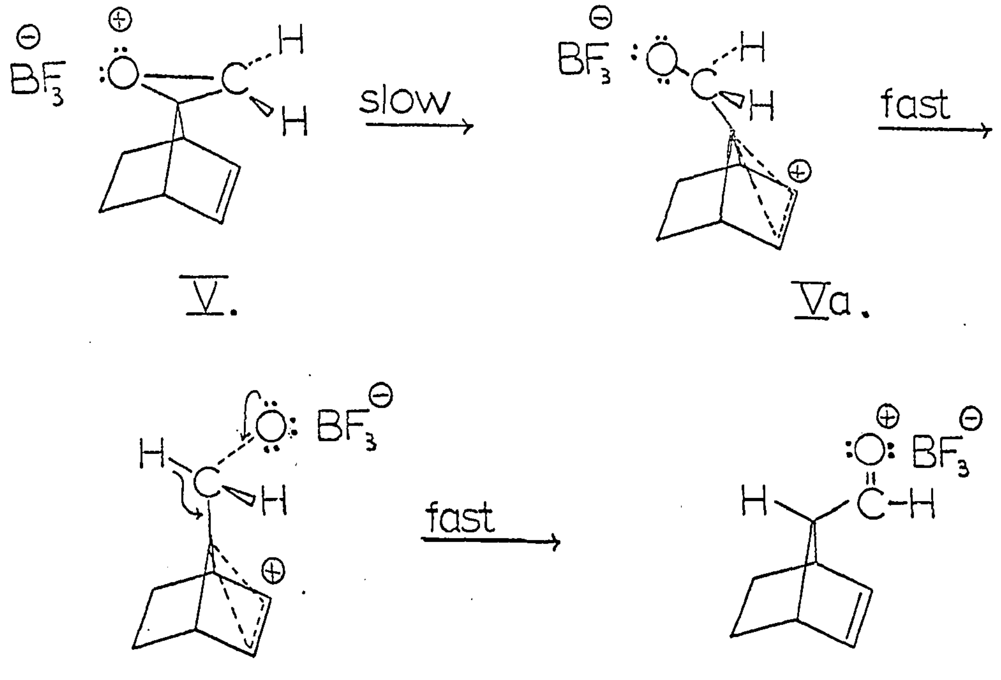
I.

II.



III. IV.

Bly and Bly report the stereospecific rearrangement of V by heat or Lewis acids to VI with retention of configuration at the migration terminus (6). Obviously, this rearrangement cannot follow a concerted path. Bly and Bly suggest a nonconcerted path with a slow first step which would be analogous to that of an acid-catalyzed epoxide cleavage (1) and a fast second step which would resemble that of a nonconcerted pinacol rearrangement (8). Thus the first, and probably rate-determining, step would consist of heterolysis of the C_7-O bond, assisted by the coordinated Lewis acid and by a backside "push" from the π-electrons to form the intermediate ion, Va. The C_7-C_8 bond of this intermediate could then rotate with a minimum of steric interference to a conformation that would allow the migrating nucleophile (hydride) to attack the delocalized carbonium ion from the preferred <u>anti</u> side (6).

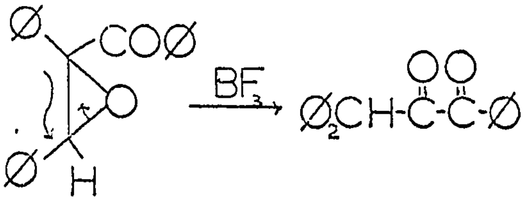


V. Va. VI.

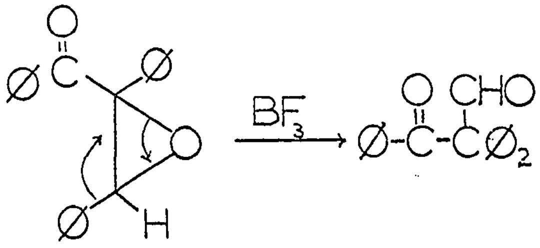
House and Reif have shown that a pair of geometrical isomers rearrange to different products, thereby favoring the concerted mechanism (9). In a two stage mechanism, one would expect the two epoxides (VII, VIII) to open in the same direction giving the same intermediate carbonium ion and therefore the same product. Considering a concerted mechanism, it can be shown that the <u>trans</u>-isomer (VIII) is sterically hindered from rearranging to the same product as the <u>cis</u>-isomer (VII) due to the unfavorable <u>cis</u> orientation of the bulky groups.

The relative migratory aptitude of R groups appears to be aryl>acyl>hydrogen>ethyl>methyl (1).

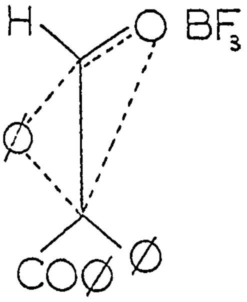
VII.



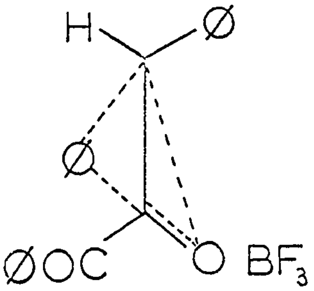
VIII.



VII.
cis

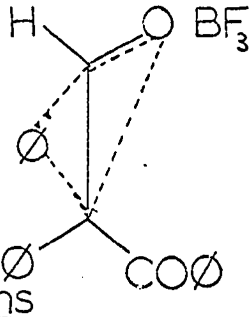


possible

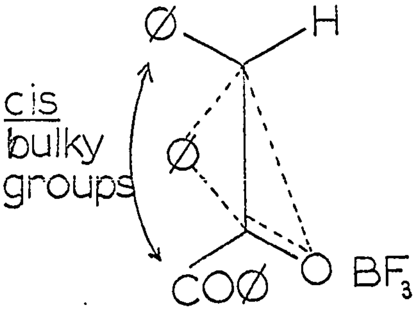


possible, apparently favored

VIII.
trans

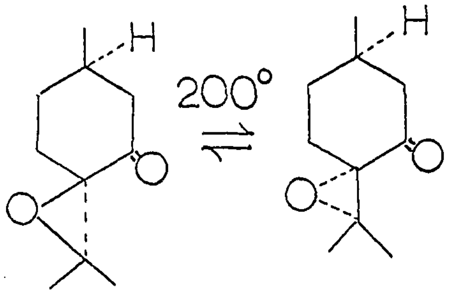


possible

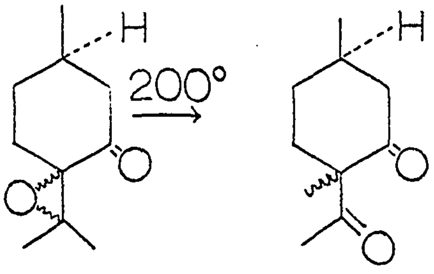


not favored

Reusch and Johnson have reported that the diastereomeric pulegone oxides undergo thermal interconversion (10) and rearrangement with an alkyl shift (11).

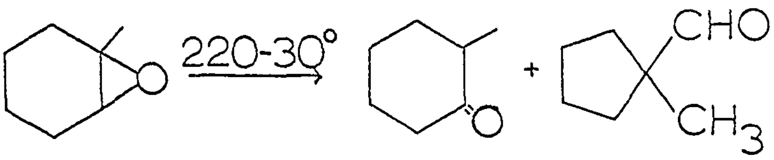


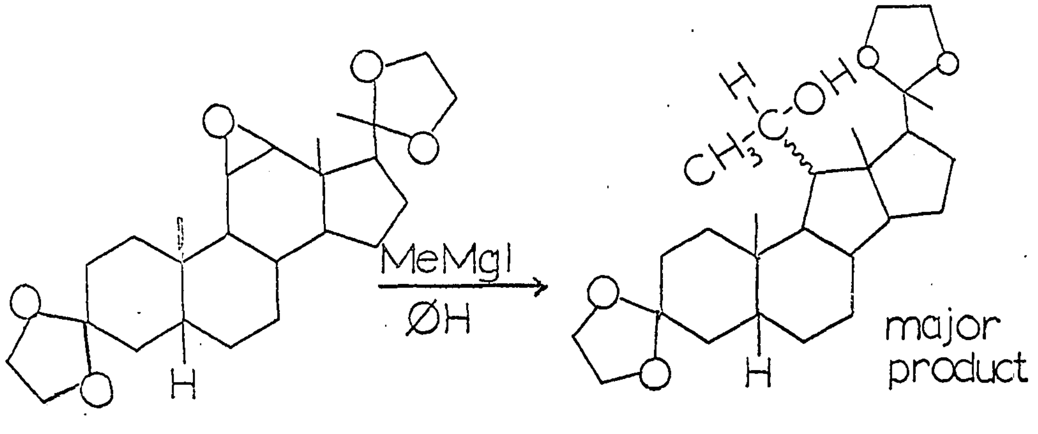
with decomposition



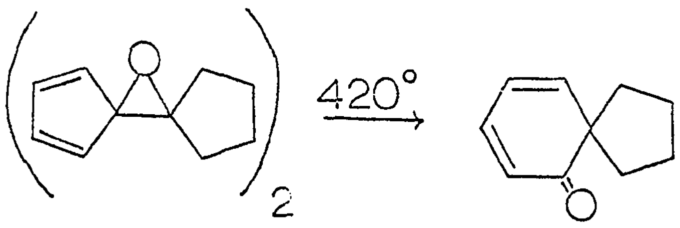
75%

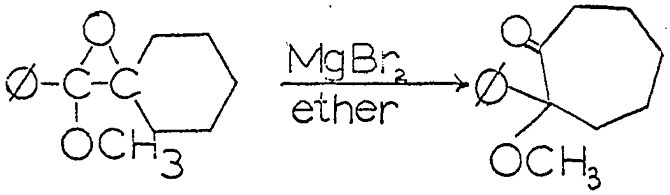
Thermal and acid catalyzed rearrangements involving cyclic epoxides can lead to ring expansion or contraction (12, 13, 14, 15).





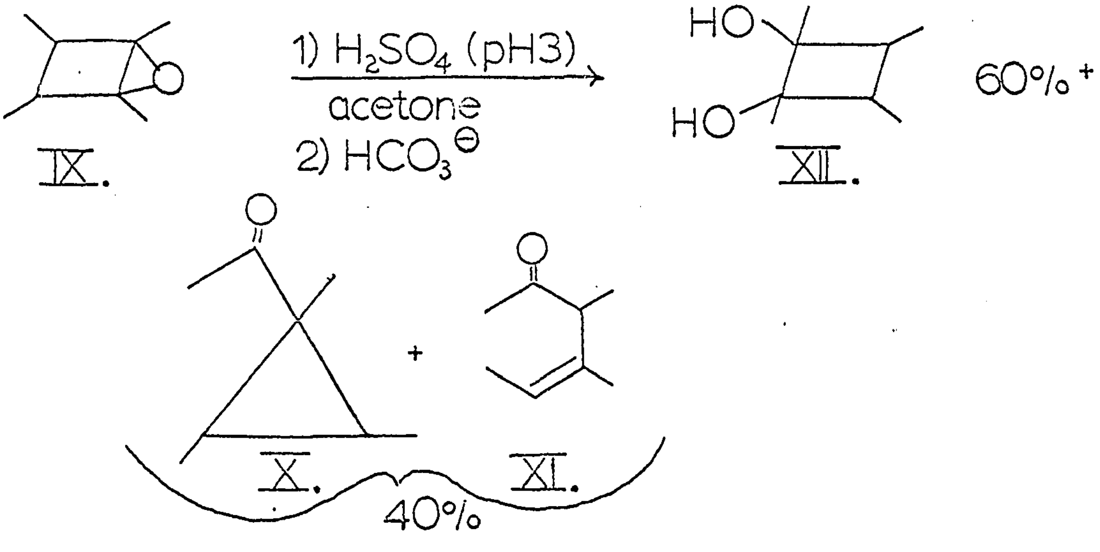
11β,12β Steroid



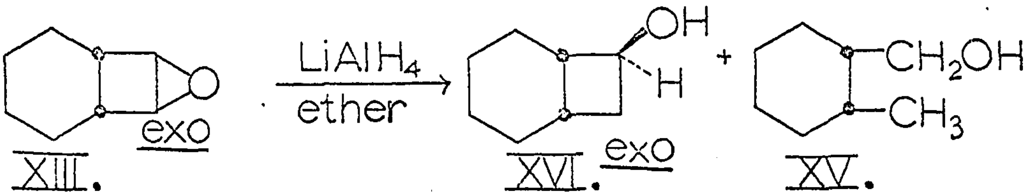


Rearrangements of cyclobutene oxides

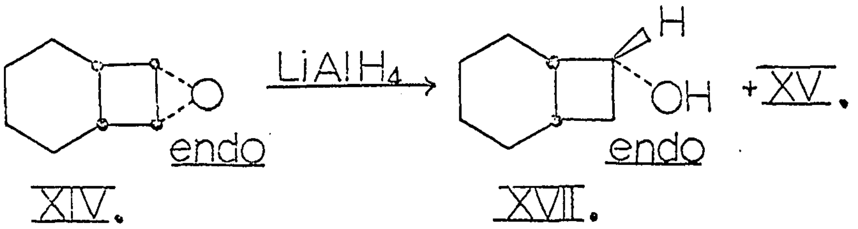
Criegee and Noll reported the acid or pyrolytic rearrangement of 1,2,3,4,-tetramethylcyclobutene oxide (IX) to two unexpected products (X, XI) besides the desired diol (XII) (16). The unsaturated ketone (XI) could easily arise via acid catalyzed ring opening of the cyclopropyl ketone (X).



Cope and Gleason reported that the lithium aluminum hydride reduction of both exo- and endo-bicyclo(4.2.0)oct-7-ene oxide (XIII and XIV, respectively) gave almost equal amounts of rearranged cis-2-methylcyclohexanemethanol (XV) and the corresponding bicyclo(4.2.0)octan-7-ol (exo-, XVI, from exo-oxide, XIII; endo-, XVII, from endo-oxide, XIV) (17).



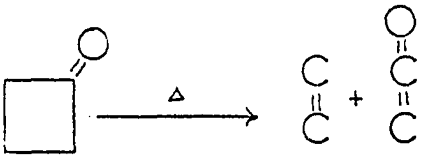
XIII. XVI. XV.



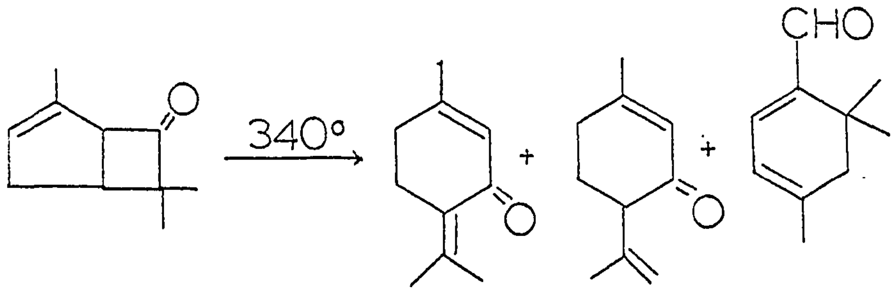
XIV. XVII.

Pyrolysis of cyclobutanones

Cyclobutanone has been reported to rearrange to ethylene and ketene at 333-73° via a non-free radical mechanism (propylene, toluene, or nitric oxide did not decrease the rate) (18). A bi-radical decomposition was suggested.

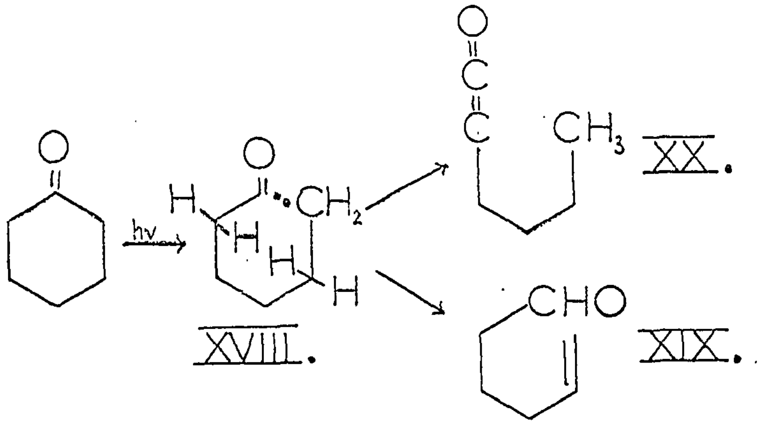


Beereboom reported the pyrolysis of a cyclobutanone to three products (19). No mechanism was offered.

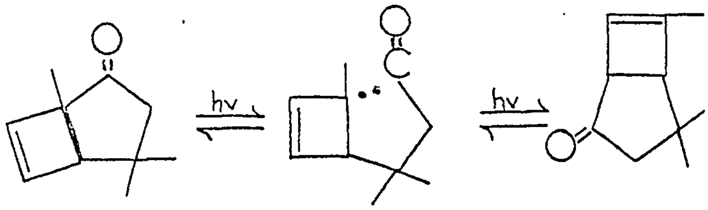


Photochemical Rearrangements of Cyclic Ketones

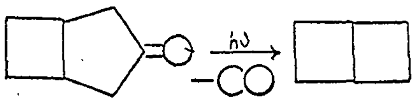
The photochemical excitation of the carbonyl group of a simple cycloalkanone often leads to fission of the bond between the carbonyl group and the more heavily substituted α-carbon (20). This "α-cleavage" leads to the formation of unsaturated aldehydes and/or saturated ketenes. Schematically, using cyclohexanone as an example, the α-cleavage may be viewed as a homolytic fission to an intermediate (XVIII) which can undergo intramolecular abstraction of a hydrogen atom at the carbon adjacent to the alkyl radical giving the unsaturated aldehyde (XIX) or from the carbon adjacent to the acyl radical giving the ketene (XX) (20). Evidence to support the mechanism for both aldehyde formation (21) and ketene formation (22) has been reported.



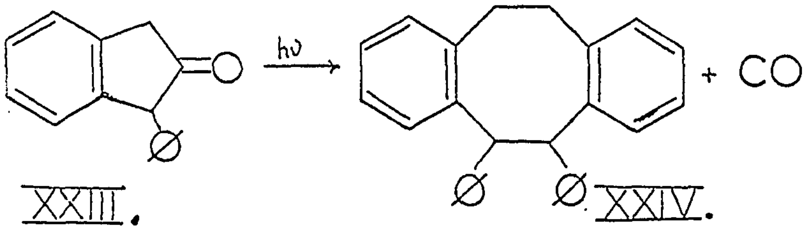
Cycloalkanones can also isomerize without proton abstraction via α-cleavage (23).



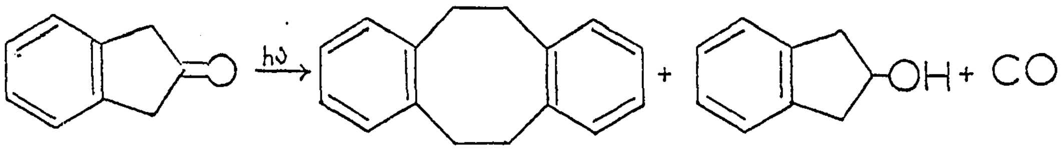
Photolysis can also lead to loss of carbon monoxide leaving a biradical that can further react. Thus bicyclo-(3.2.0)heptan-2-one (XXI) gives bicyclo(2.2.0)hexane (XXII) in low yield (24). The stability of the decarbonylated diradical is apparently a deciding factor in product formation. The irradiation of XXIII gives XXIV, the decarbonylated diradical apparently more willing to dimerize than form the strained benzocyclobutane. The α-phenyl group probably aids the decarbonylation step in stabilizing the resulting radical since the analogous XXV gives only 5% of XXVI (compared to the formation of 80% of XXIV), the major product being the reduced ketone, XXVII (25).



XXI. XXII.



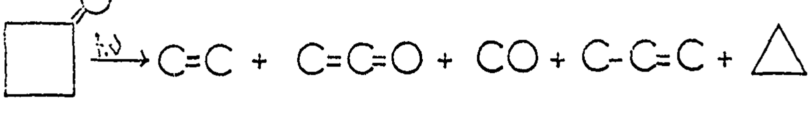
XXIII. XXIV.



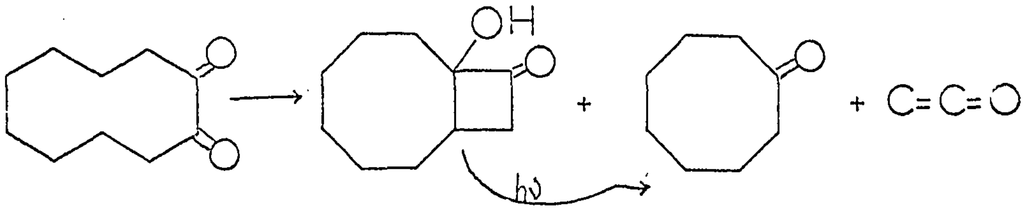
XXV. XXVI. XXVII.

Photolysis of cyclobutanones and norcamphor

Benson and Kistiakowsky reported that photolysis of cyclobutanone gave ethylene and ketene as well as carbon monoxide and C_3H_6 hydrocarbons (26). This work was confirmed by Blacet and Miller who concluded that the primary process is not free radical in nature (27).

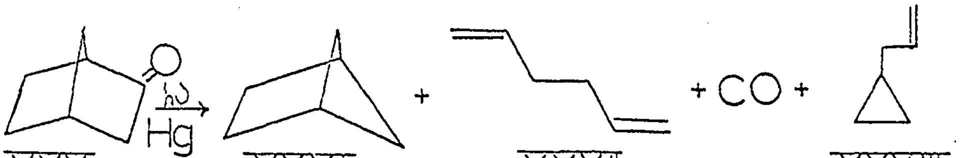


Irradiation of 1,2-cyclodecanedione (XXVIII) gives 1-hydroxybicyclo(6.2.0)decan-10-one (XXIX) and a small amount of cyclooctanone and ketene, presumably formed from secondary photolysis of the bicyclobutanone, XXIX (28).

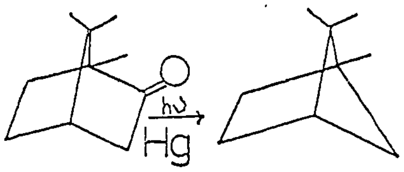


XXVIII. XXIX.

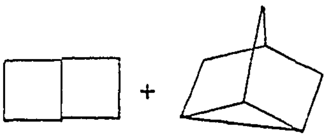
Srinivasan reported the vapor phase photolysis of norcamphor (XXX) gave bicyclo(2.2.1)hexane (XXXI), 1,5-hexadiene (XXXII) and carbon monoxide (29). The mercury photosensitized decomposition in a quartz container gave the above products and allyl cyclopropane (XXXIII), as well as minor amounts of bicyclo(2.2.0)hexane (XXII), nortricyclene (XXXIV) and an unsaturated aldehyde that could not be identified (30). The photolysis of a deuterated sample of norcamphor suggested direct loss of carbon monoxide. Irradiation of optically active d-camphor (XXXV) gave a similar bicyclic compound (XXXVI) which was optically active (30).



XXX. XXXI. XXXII. XXXIII.



XXXV. XXXVI.



XXII. XXXIV.

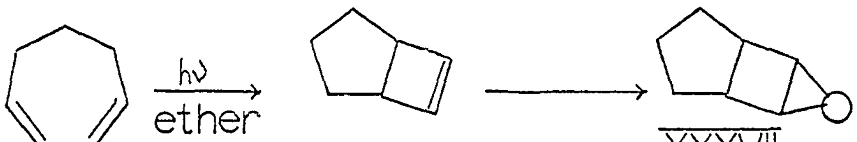
RESULTS AND DISCUSSION

The Pyrolysis of Cyclobutene Oxides

For the study of cyclobutene oxides, bicyclo(3.2.0)hept-6-ene oxide (XXXVII) and bicyclo(4.2.0)oct-7-ene oxide (XIII) are ideal compounds in that they are symmetrical and held in a fixed conformation, thus giving fewer possibilities for initial bond breakage and fewer products by rearrangement.

Bicyclo(3.2.0)hept-6-ene oxide (XXXVII) was prepared by peracid oxidation of the bicyclic photoproduct of 1,3-cycloheptadiene (infrared: 3050, 951, 854, 837 and 788 cm^{-1}, Figure 2, p. 20). Cope and Gleason reported that the peracid oxidation of bicyclo(4.2.0)oct-7-ene gives both exo- and endo-epoxides with the exo isomer favored 87:13 (17). The more rigid bicyclo(3.2.0)hept-6-ene would be expected to give an even greater predominance of the exo-epoxide.

Pyrolysis was effected by dropwise addition of the epoxide to a column of glass helices in a temperature control oven under slow nitrogen flow (see Figure 1, p. 16). Optimum temperature was determined to be 420° for complete conversion and lowest number of products as determined by analysis by gas phase chromatography utilizing a Perkin-Elmer RX column.



XXXVII

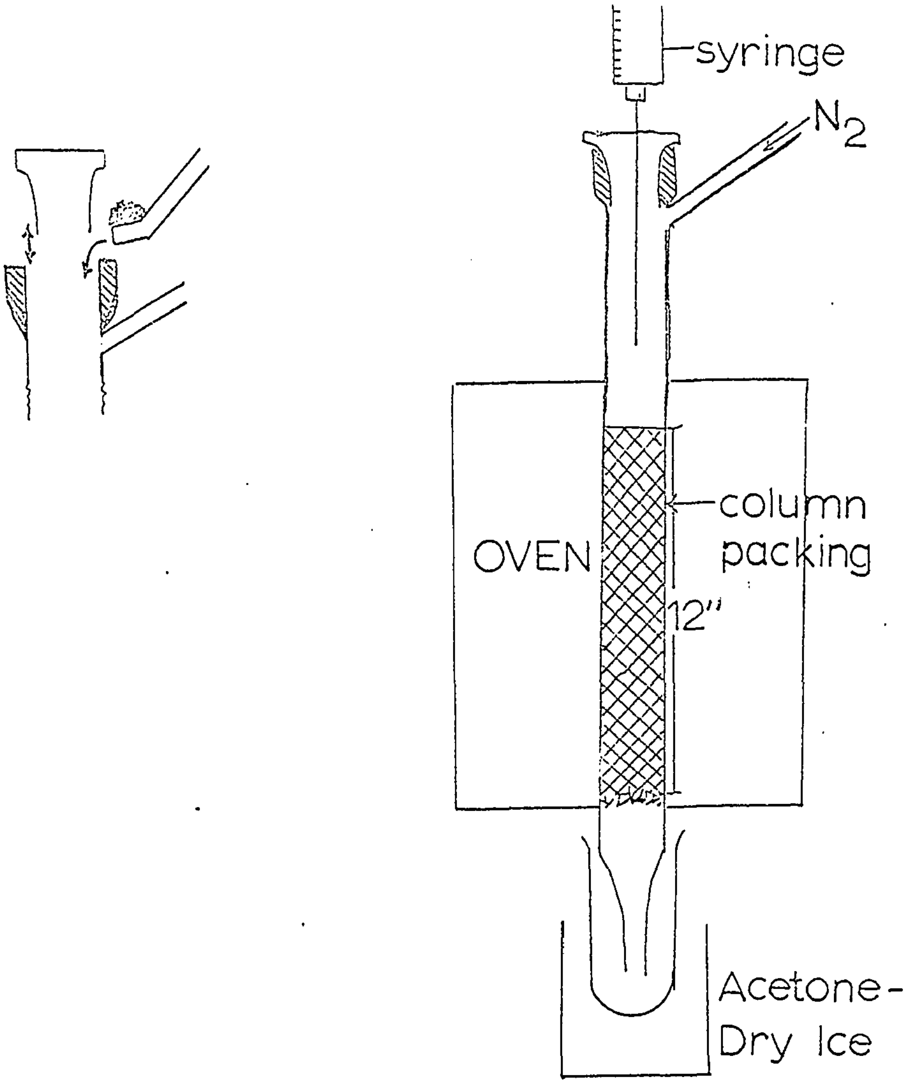


Figure 1. Pyrolysis apparatus

The percentages of products given were based on integration of the peak area compared to total peak area on the gas phase chromatogram. From a large number of high and low boiling products, a sample of the major constituent (50%) was isolated by collection from the gas chromatograph. The infrared spectrum (Figure 2, p. 20) suggested an unsaturated aldehyde with absorption at 2820 and 2720 cm^{-1} (aldehydic proton), 1725 cm^{-1} (carbonyl), and 3080, 1615 and 910 cm^{-1} (double bond). The infrared assignments used throughout this thesis are based on two standard texts (31, 32). The aldehydic proton appeared as a triplet (J~2 c.p.s.) at 9.7 p.p.m. in the nuclear magnetic resonance spectrum suggesting a methylene group adjacent to the aldehyde (Figure 3, p. 22). Integration of the nuclear magnetic resonance spectrum showed two olefinic protons (5.7 p.p.m.) relative to a total of ten protons. The nuclear magnetic resonance assignments used in this thesis are based on two reference texts (33, 34) and information supplied by Dr. O. L. Chapman and Dr. R. W. King. The aldehyde was identified as Δ^2-cyclopentenylacetaldehyde (XXXVIII) by comparison with an authentic sample (see below) and by reduction to the corresponding alcohol and comparison with known 2-(Δ^2-cyclopentenyl)ethanol (XXXIX). The infrared spectrum of the aldehyde, XXXVIII, was superimposable with that of an authentic sample, prepared by photolysis of norcamphor (see p. 60). The 2,4-dinitrophenylhydrazone of the aldehyde had m.p. 104-5° (literature (35) m.p. 98-9°). A mixed melting point showed no depression.

Reduction of XXXVIII with lithium aluminum hydride in ether gave a primary alcohol (3675 and 1056 cm^{-1}) which was still unsaturated (3080, 1615, 910 cm^{-1}). Integration of the nuclear magnetic resonance spectra showed two hydroxymethylene protons at 3.6 p.p.m. (triplet, J~6.7 c.p.s.) relative to two olefinic protons at 5.6 p.p.m. (multiplet) and to a total of twelve protons (Figure 3, p. 22). The known alcohol, XXXIX, was prepared by lithium aluminum hydride reduction of Δ^2-cyclopentenylacetic acid (XL), synthesized via the procedure of Noller and Adams (36). The infrared spectrum of the primary alcohol was superimposable with that of XXXIX (Figure 2, p. 20). The α-naphthylurethan had m.p. 81-3°. A mixed melting point showed no depression.

One unsaturated ether (2%) was collected (infrared: 3050, 1653, 1640, 1460, 1130 and 1028 cm^{-1}), but enough material could not be obtained to further characterize it.

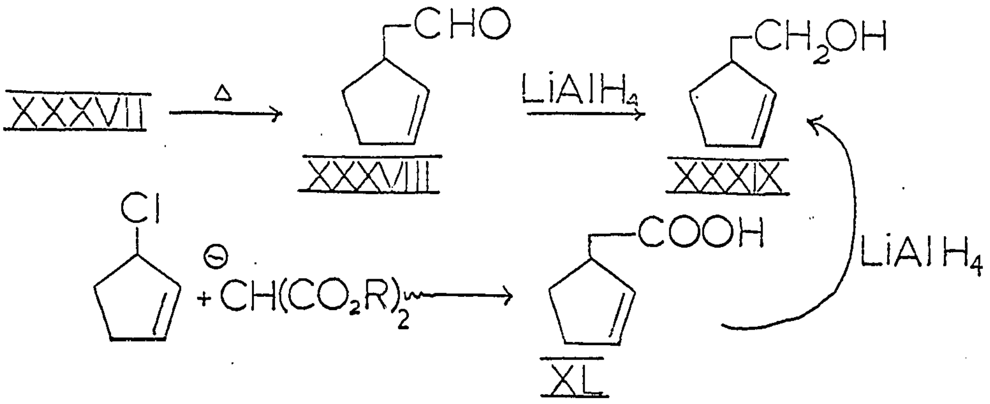
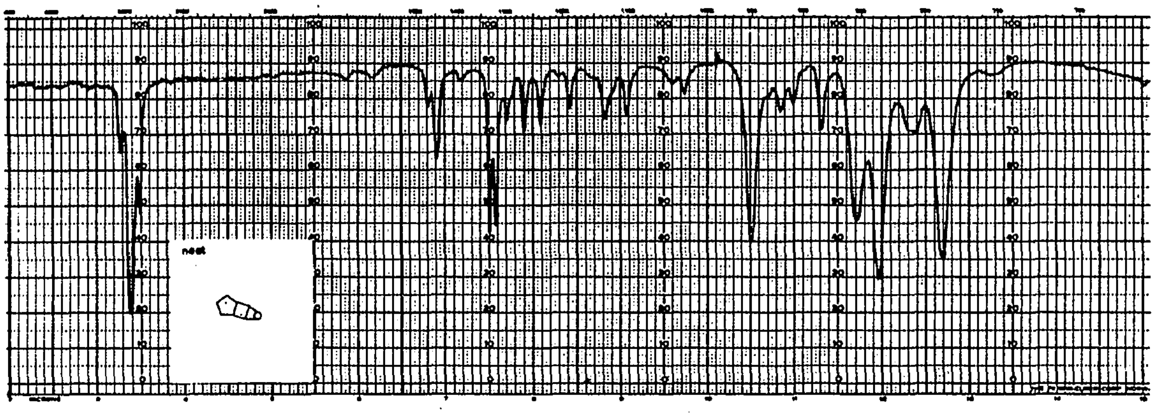


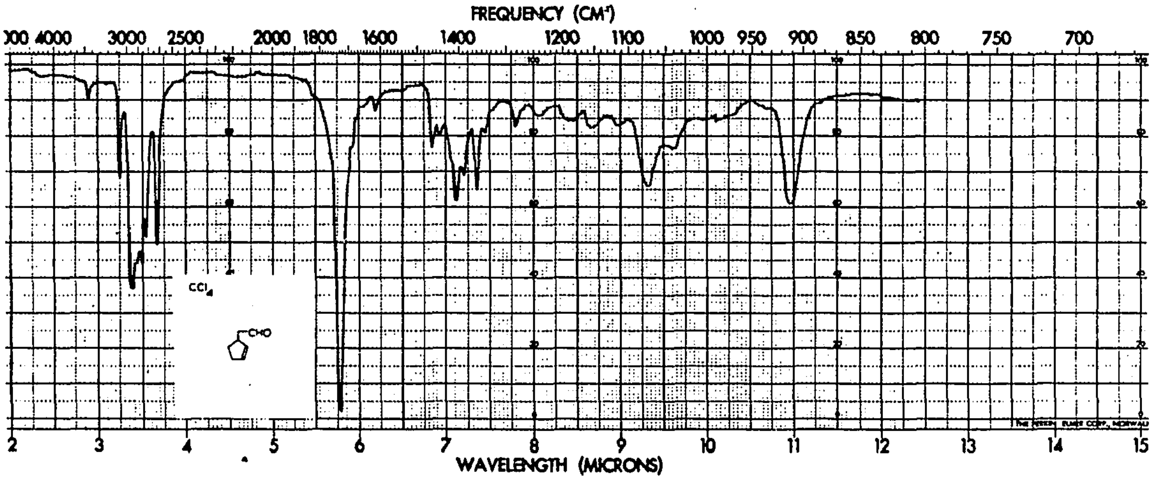
Figure 2. Infrared spectra

Top - Bicyclo(3.2.0)hept-6-ene oxide (XXXVII)

Middle - Δ^2-Cyclopentenylacetaldehyde (XXXVIII)

Bottom - Top, 2-(Δ^2-Cyclopentenyl)ethanol (XXXIX)
Bottom, Authentic sample


neat


FREQUENCY (CM⁻¹)
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CCl4
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

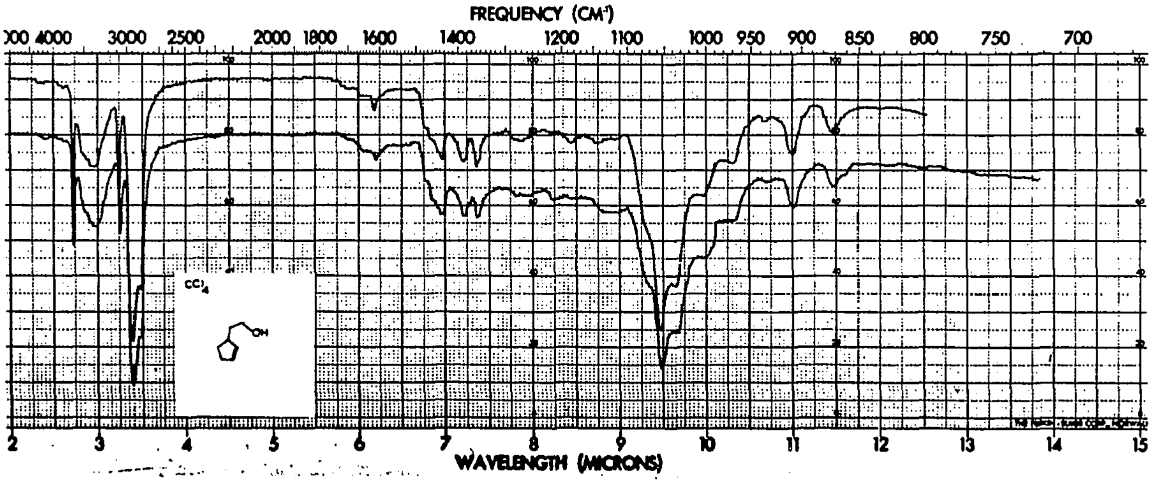
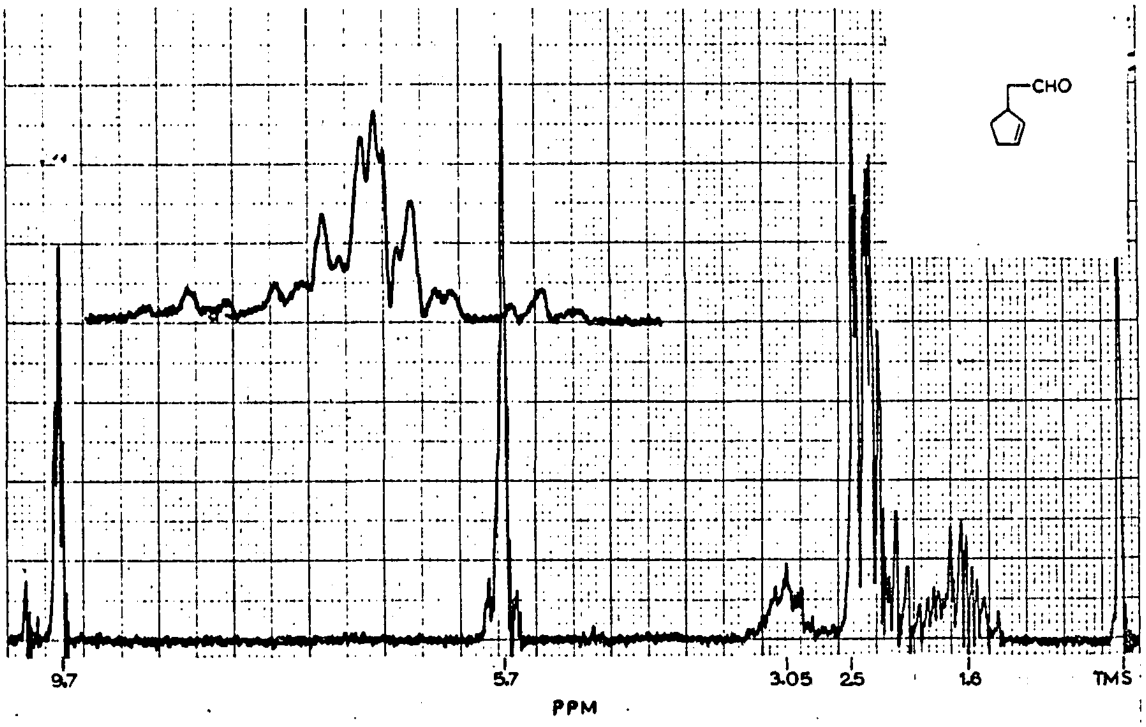
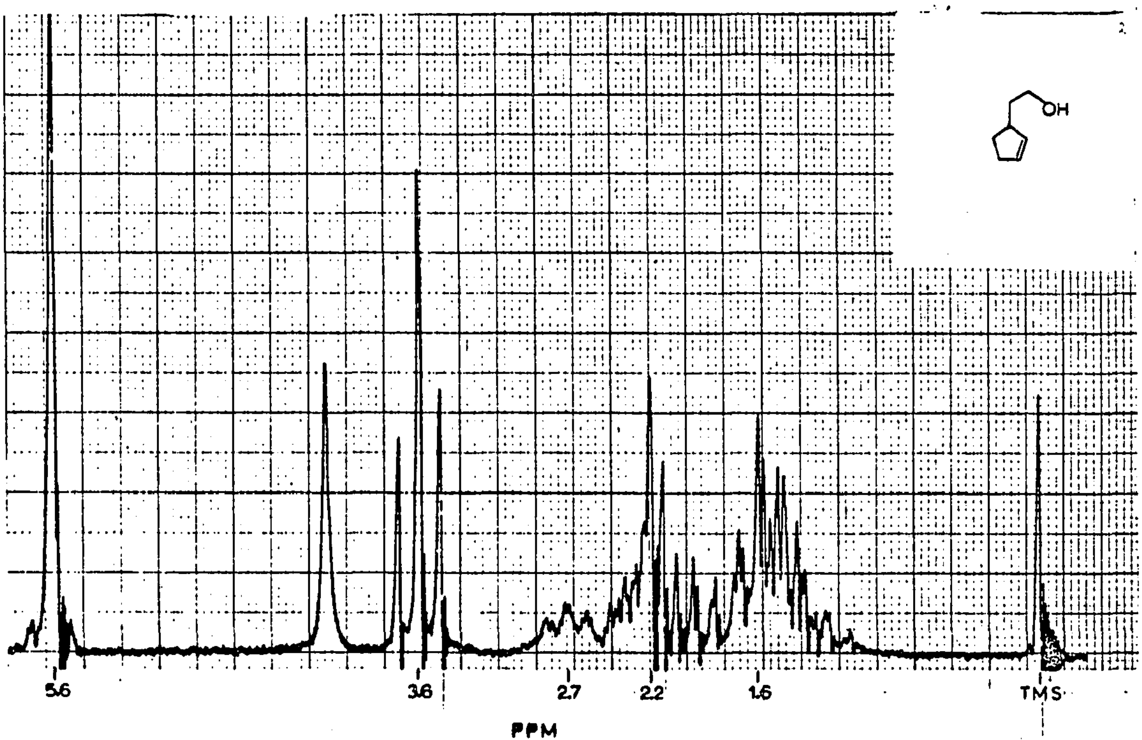

FREQUENCY (CM⁻¹)
00 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl4
OH
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 3. Nuclear magnetic resonance spectra

Top - Δ^2-Cyclopentenylacetaldehyde (XXXVIII)
Bottom - 2-(Δ^2-Cyclopentenyl)ethanol (XXXIX)

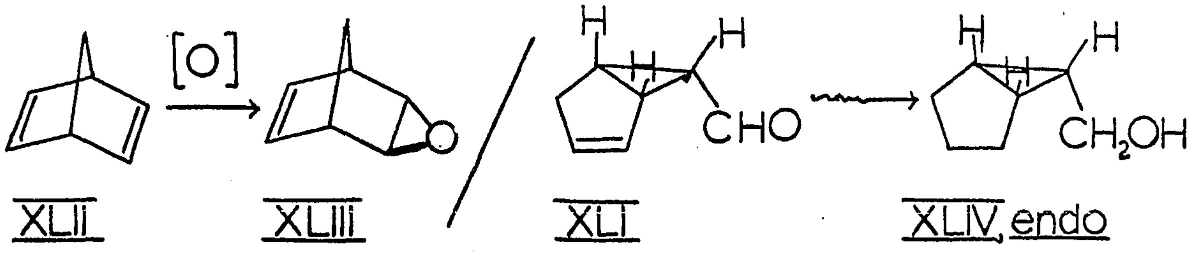

CHO
9.7
5.7
3.05
2.5
1.6
TMS
PPM


OH
5.6
3.6
2.7
2.2
1.6
TMS
PPM

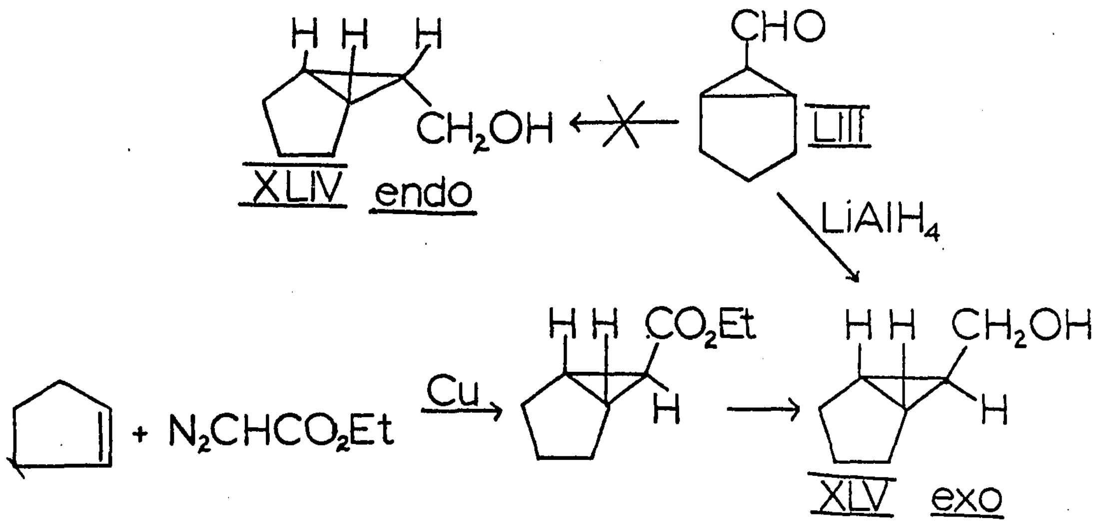
One of the minor products from the pyrolysate (5%) was isolated in impure form. The nuclear magnetic resonance spectrum of this material showed a sharp aldehyde doublet ($J \sim 5$ c.p.s.) at 9.2 p.p.m., no olefinic protons and a methylene region that extended to 1.0 p.p.m. The infrared spectrum showed aldehyde absorption (2830 and 2720 cm^{-1}), two carbonyl absorptions (1710 and 1690 cm^{-1}) and cyclopropyl absorption (3050 and 1030 cm^{-1}). It seemed possible that the major substituent of this mixture was bicyclo(3.1.0)hexane-6-carboxaldehyde, either endo- or exo- or a mixture of both isomers. The mixture was reduced with lithium aluminum hydride to the more stable alcohols. The nuclear magnetic resonance spectrum showed two sets of hydroxymethylene doublets ($J \sim 7$ c.p.s.) at 3.3 and 3.5 p.p.m. in an area ratio of 2:1 respectively. Both endo- and exo-6-hydroxymethylenebicyclo(3.1.0)-hexane were synthesized for comparison.

Meinwald, Labana and Chadha reported the formation of the rearranged bicyclo(3.1.0)hex-2-ene-endo-6-carboxaldehyde (XLI) from the attempted monoepoxidation of norbornadiene (XLII) (37). Repetition of the peracid oxidation followed by immediate workup and flash distillation gave an unstable semi-solid with spectral properties which suggested that it was a monoepoxide of norbornadiene (XLIII). The nuclear magnetic resonance spectrum showed two olefinic protons (triplet, $J \sim 1.5$ c.p.s.) at 3.5 p.p.m., a two proton singlet (epoxide protons) at 3.25 p.p.m., two bridgehead protons at 2.9 p.p.m. and two bridge protons at 1.3 p.p.m. The infrared spectrum showed the presence of an epoxide linkage (852 cm^{-1}). These results were later confirmed by Meinwald and coworkers in a personal communication. Distillation at higher temperatures did afford the rearranged aldehyde (XLI) which was converted to _endo_-6-hydroxymethylenebicyclo(3.1.0)hexane (XLIV) via silver oxide oxidation, hydrogenation in ethyl acetate with Adams catalyst and lithium aluminum hydride reduction.

Ethyl bicyclo(3.1.0)hexane-_exo_-6-carboxylate was prepared by addition of diazoacetic ester to cyclopentene as reported by Meinwald, Labana and Chadha (37). In the closely related case of the copper-catalyzed addition of diazoacetic ester to cyclohexene, it has been shown that steric discrimination takes place favoring the _exo_ adduct over the _endo_ by a 16:1 ratio (38). Analysis by gas chromatography showed that the resulting product was mainly one compound with two impurities. Without further purification, this was reduced to the corresponding _exo_-6-hydroxymethylenebicyclo(3.1.0)-hexane (XLV) with lithium aluminum hydride in ether.

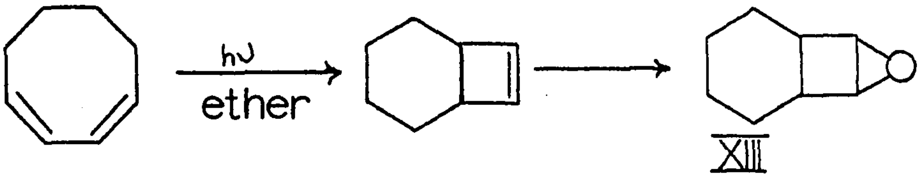


XLII XLIII XLI XLIV, endo



The alcohols were analyzed by gas phase chromatography on a THEED column at 125° and 150°. Under these conditions both *exo* and *endo* alcohols could be resolved. The product from the synthesis of the *endo* alcohol (XLIV) described above was shown to be one isomer. The product from the synthesis of the *exo* alcohol (XLV) was shown to contain both *exo* and *endo* isomers in a ratio of greater than 10:1 in favor of the *exo* isomer as expected. The major product from the reduction of the aldehyde obtained from the pyrolysis of XXXVII was shown to be the *exo* alcohol by comparison of retention times on the gas chromatograph. The *endo* alcohol was not present. Therefore, the bicyclic aldehyde obtained from the pyrolysis of XXXVII is bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde (LIII). Samples of these alcohols were collected from the gas chromatograph. The infrared spectrum of the reduced aldehyde obtained from the pyrolysis of XXXVII was superimposable with that of synthetic XLV (3620, 3010, 2930, 2860, 1470, 1448, 1418, 1380, 1126, 1067, 1052, 1028, 1015, 993, 888, 871 and 845 cm^{-1}) and differed from synthetic XLIV (3620, 3010, 2930, 2860, 1480, 1448, 1410, 1380, 1330, 1182, 1038, 1015, 901 and 866 cm^{-1}; Figure 4, p. 28). The nuclear magnetic resonance spectrum of XLV had a sharp hydroxymethylene doublet (J~7 c.p.s.) at 3.3 p.p.m. and that of XLIV had a doublet (J~7 c.p.s.) at 3.5 p.p.m. (Figure 5, p. 30). Both spectra integrated for twelve total protons relative to two hydroxymethylene protons.

Bicyclo(4.2.0)oct-7-ene oxide (XIII) was prepared by peracid oxidation of the bicyclic photoproduct of 1,3-cyclooctadiene (infrared: 3040, 942, 825, 809 and 760 cm^{-1}; Figure 6, p. 34).



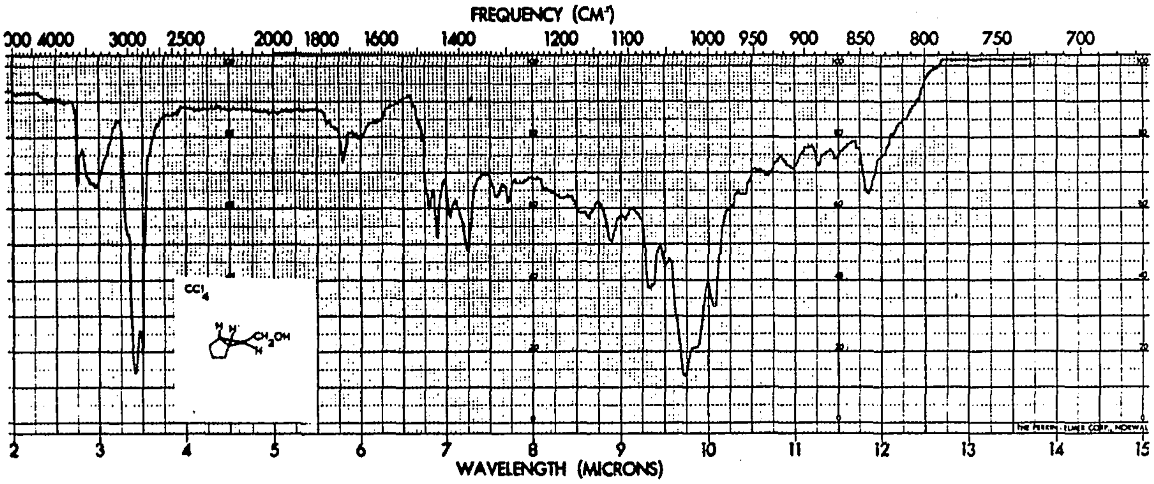
Pyrolysis of XIII at 400° was extremely clean giving only three products. The minor low boiling product (13%) appeared to be 1-methylcyclohexene (XLVI) by a comparison of retention times on the gas chromatograph. A sample was collected from the gas chromatograph for spectral analysis. The nuclear magnetic resonance spectrum showed one olefinic proton (5.3 p.p.m.) relative to twelve total protons.

Figure 4. Infrared spectra

Top - *Exo*-6-hydroxymethylenebicyclo(3.1.0)hexane (XLV) from the reduction of bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde (LIII)

Middle - Authentic sample of *exo*-6-hydroxymethylenebicyclo(3.1.0)hexane (XLV)

Bottom - *Endo*-6-hydroxymethylenebicyclo(3.1.0)hexane (XLIV)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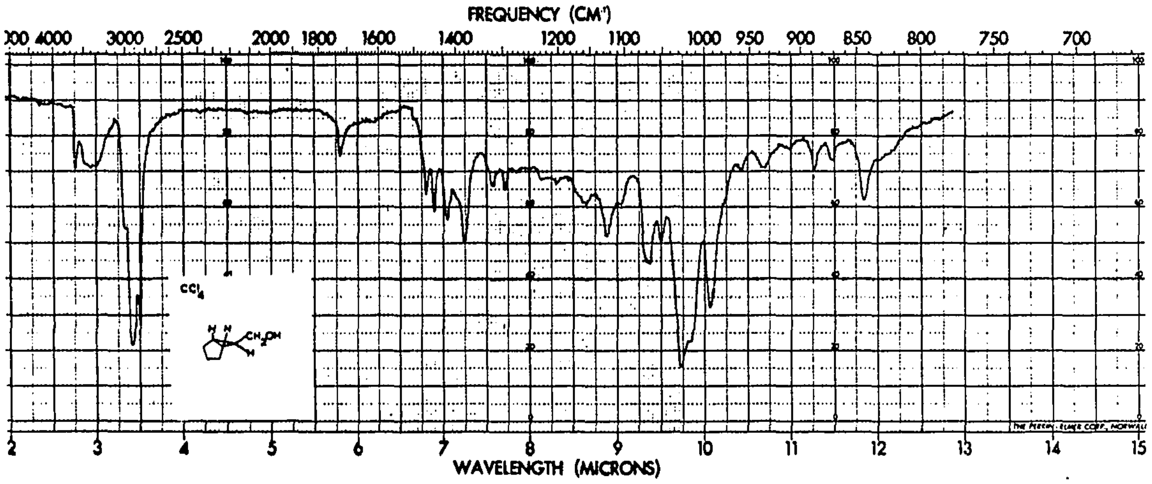
CCl4
H H
CH2OH
H
WAVELENGTH (MICRONS)
2 3 4 5 6 7 8 9 10 11 12 13 14 15
THE PERKIN-ELMER CORP., NORWALK


FREQUENCY (CM⁻¹)
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CH2OH
H
WAVELENGTH (MICRONS)
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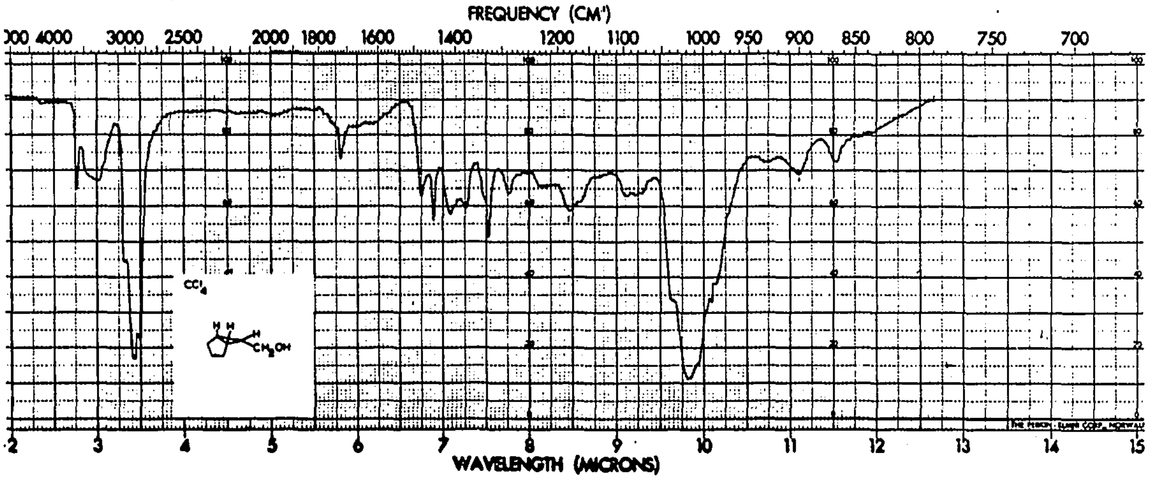
THE PERKIN-ELMER CORP., NORWALK


FREQUENCY (CM⁻¹)
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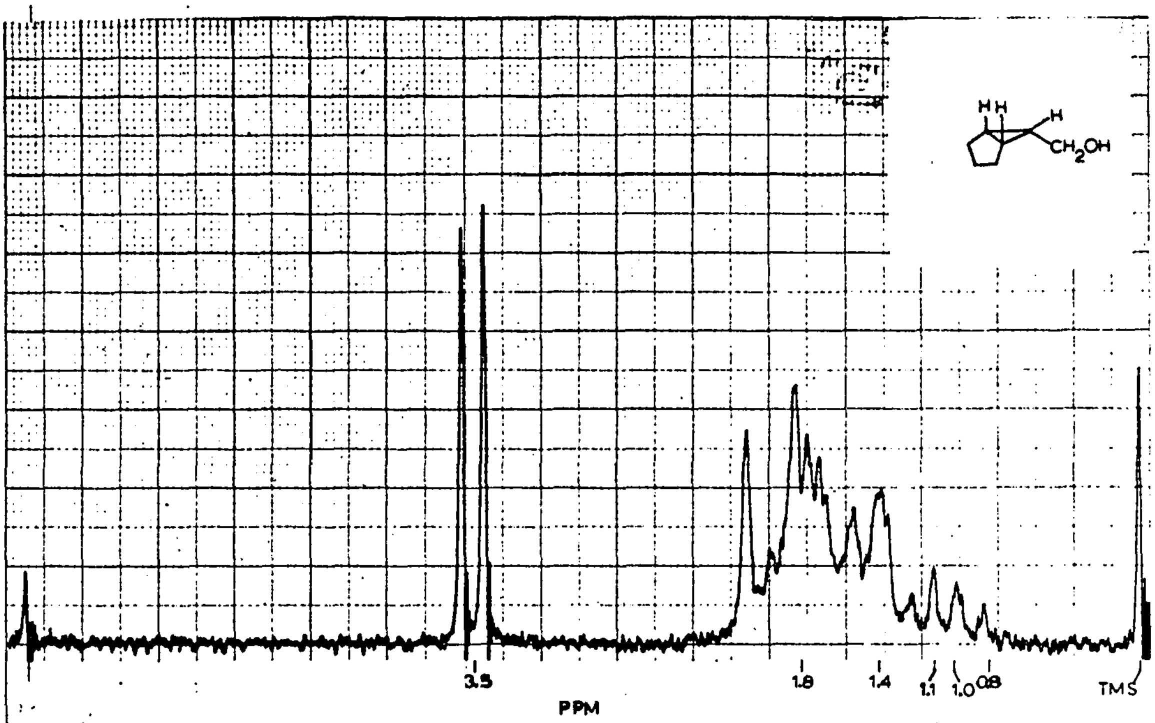
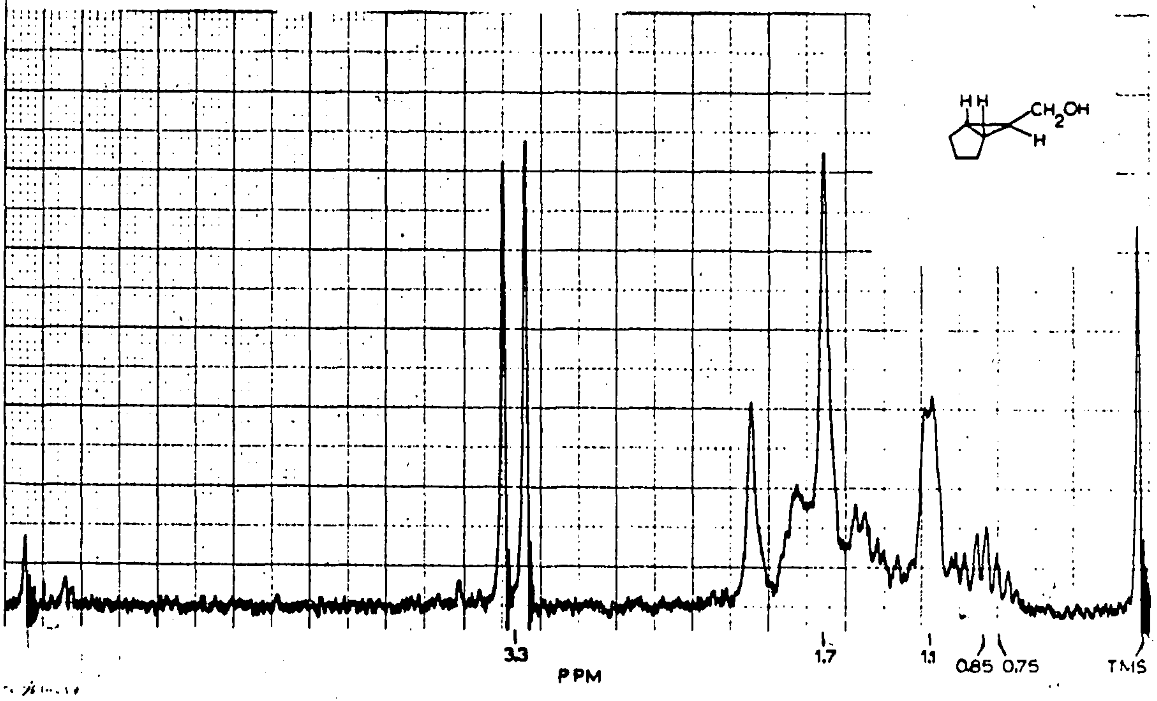
CCl4
H H
H
CH2OH
WAVELENGTH (MICRONS)
2 3 4 5 6 7 8 9 10 11 12 13 14 15
THE PERKIN-ELMER CORP., NORWALK

Figure 5. Nuclear magnetic resonance spectra

Top - *Endo*-6-hydroxymethylenebicyclo(3.1.0)-hexane (XLIV)

Bottom - *Exo*-6-hydroxymethylenebicyclo(3.1.0)-hexane (XLV)


H H
H
CH2OH
3.5
1.8
1.4
1.1
1.0
0.8
TMS
PPM


H H
CH2OH
H
3.3
1.7
1.1
0.85
0.75
TMS
PPM

Comparison of the infrared spectrum with that of known XLVI (prepared by reaction of methyl Grignard reagent with cyclohexanone and acid dehydration of the resulting alcohol) confirmed the identity. Product percentages were determined by cutting out peak areas from several gas chromatograms, then weighing the "peak" and comparing it to the weight of the other peaks and averaging the results.

The lesser of the two major products (31%) was identified as Δ^2-cyclohexenylacetaldehyde (XLVII). The infrared spectrum was consistent with this structure (aldehydic hydrogen, 2860 and 2710 cm^{-1}; carbonyl, 1725 cm^{-1}; double bond, 3030, 1650, 1435 and 835 cm^{-1}; Figure 6, p. 34). The nuclear magnetic resonance spectrum showed an aldehydic proton at 9.7 p.p.m. (triplet, J~2 c.p.s.) and two olefinic protons at 5.5 p.p.m. (Figure 7, p. 36). The 2,4-dinitrophenylhydrazone of XLVII had m.p. 99.5-100.5° (literature (35) m.p. 97°). The 2,4-dinitrophenylhydrazone of dihydro XLVII had m.p. 123.5-5° (reported for the 2,4-dinitrophenylhydrazone of cyclohexylacetaldehyde (39) m.p. 124-5°). To distinguish between Δ^2-cyclohexenylacetaldehyde and the possible Δ^3-isomer, the aldehyde was reduced to the corresponding alcohol with lithium aluminum hydride and compared with an authentic sample of 2-(Δ^3-cyclohexenyl)ethanol supplied by the General Electric Research Laboratories in Schenectady, New York. Though similar, the infrared spectra of the two alcohols were different. The alcohol from the reduction of XLVII had absorption at 3300, 3030, 3010, 1645, 1448, 1432, 1138, 1067, 1049, 1010, 973, 888, 835, 720, 678 and 662 cm^{-1}. The infrared spectrum of 2-(Δ^3-cyclohexenyl)ethanol had absorption at 3300, 3030, 3010, 1645, 1448, 1432, 1138, 1070, 1050, 1040, 1010, 913, 900, 868, 835 and 652 cm^{-1} (Figure 6, p. 34).

The major component of the pyrolysate (56%) appeared to be an enol ether. The infrared spectrum showed absorption at 1670, 1040, 920 and 835 cm^{-1} (Figure 8, p. 38). The ultraviolet spectrum in 95% ethanol showed λmax. 214 $m\mu$. ($\epsilon \sim 6100$). The nuclear magnetic resonance spectrum showed one olefinic proton at 5.9 p.p.m. (triplet, J~1.5 c.p.s.) and two protons on carbon bearing oxygen at 4.3 p.p.m. (triplet, J~9.5 c.p.s.) and 3.7 p.p.m. (triplet, J~8.7 c.p.s.) (Figure 9, p. 40).

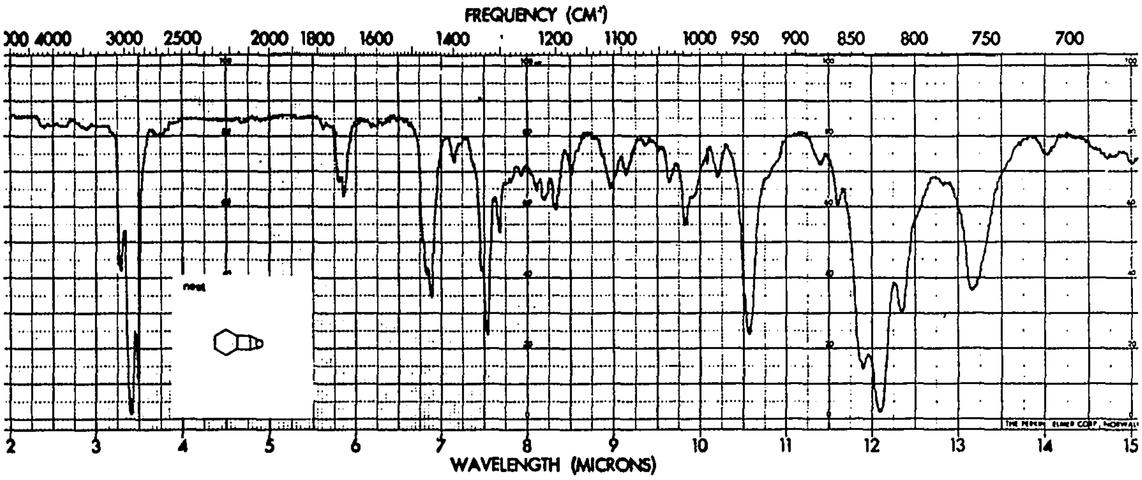
Hydrogenation in ethyl acetate with 5% platinum oxide on carbon gave a single ether believed to be 2,3-tetramethylenetetrahydrofuran (XLVIII) or 3,4-tetramethylenetetrahydrofuran (XLIX). The 2,3-tetramethylenetetrahydrofuran, synthesized from cyclohexanone and α-bromo ethyl acetate via an enamine reaction, reduction and dehydration, was not identical to the dihydro enol ether. The nuclear magnetic resonance spectrum of the dihydro enol ether was relatively simple with one broad eight proton methylene peak at 1.5 p.p.m., one broad two proton peak centered at 2.15 p.p.m., and a well split multiplet of four protons on carbon bearing oxygen centered

Figure 6. Infrared spectra

Top - Bicyclo(4.2.0)oct-7-ene oxide (XIII)

Middle - Δ^2-Cyclohexenylacetaldehyde (XLVII)

Bottom - Top, 2-(Δ^2-cyclohexenyl)ethanol
Bottom, 2-(Δ^3-cyclohexenyl)ethanol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neat
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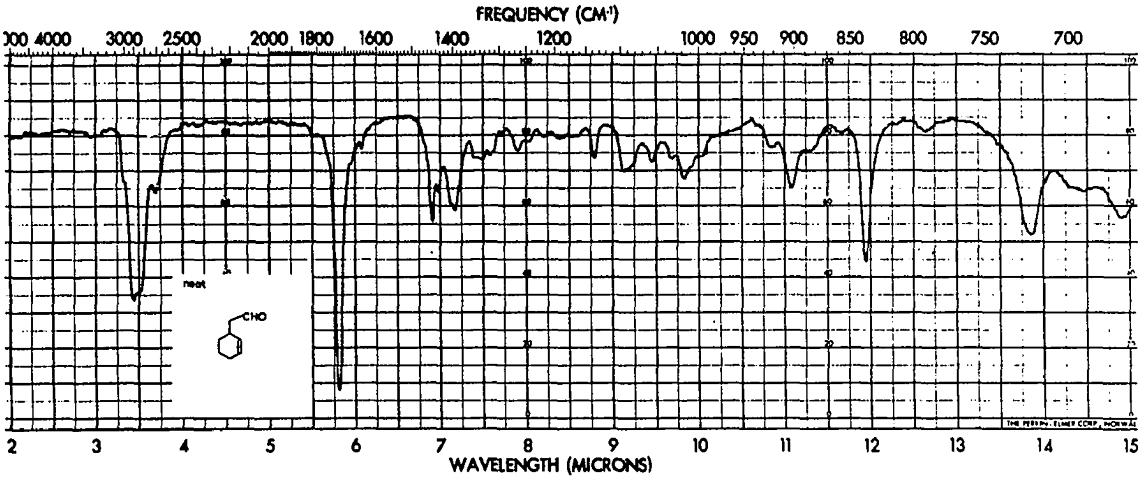
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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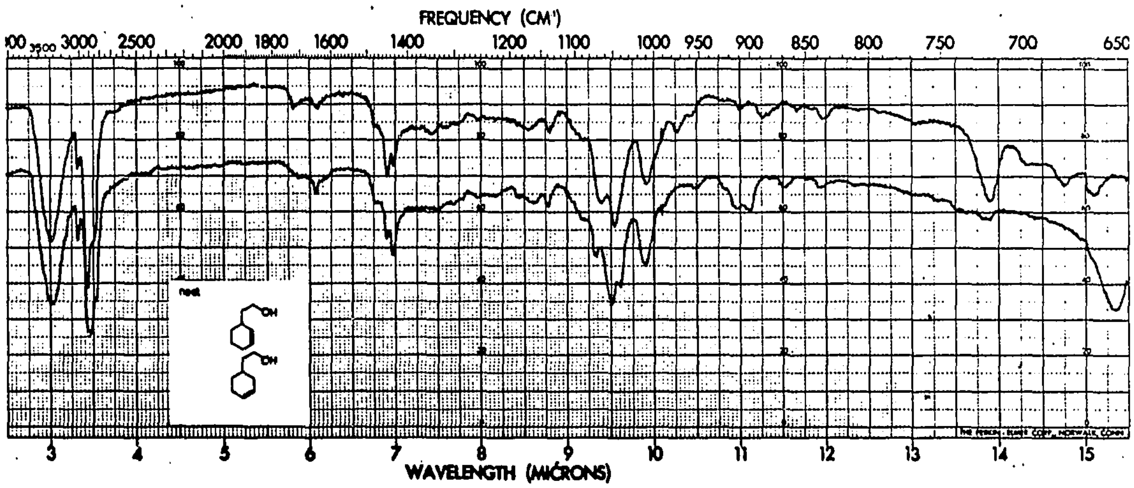
neat
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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neat
OH
OH
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 7. Nuclear magnetic resonance spectrum of Δ^2-cyclohexenylacetaldehyde (XLVII)

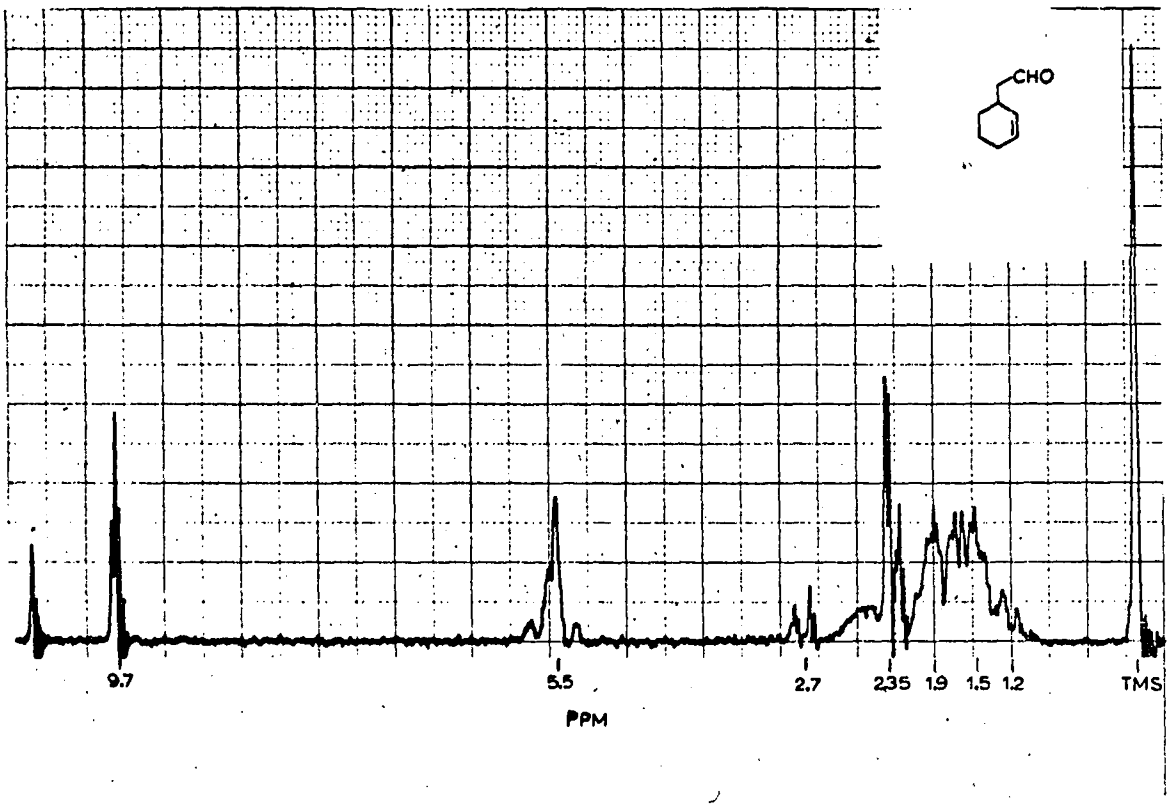
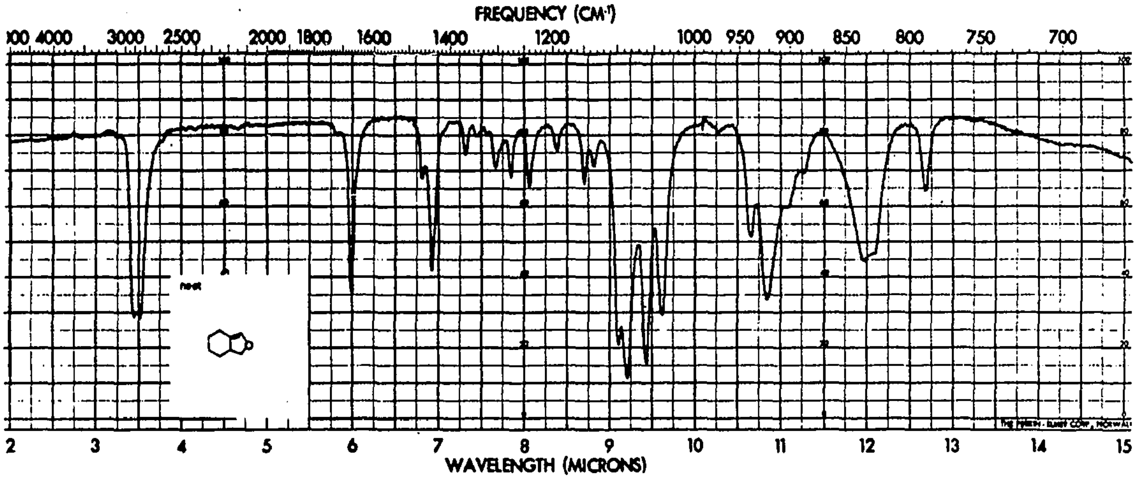

CHO
9.7
5.5
2.7
2.35
1.9
1.5
1.2
TMS
PPM

Figure 8. Infrared spectra

Top - 3,4-Tetramethylene-2,3-dihydrofuran (L)

Bottom - Top, Cis-hexahydrophthalan
Bottom, 3,4-Tetramethylene-tetrahydrofuran (XLIX)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
neat
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

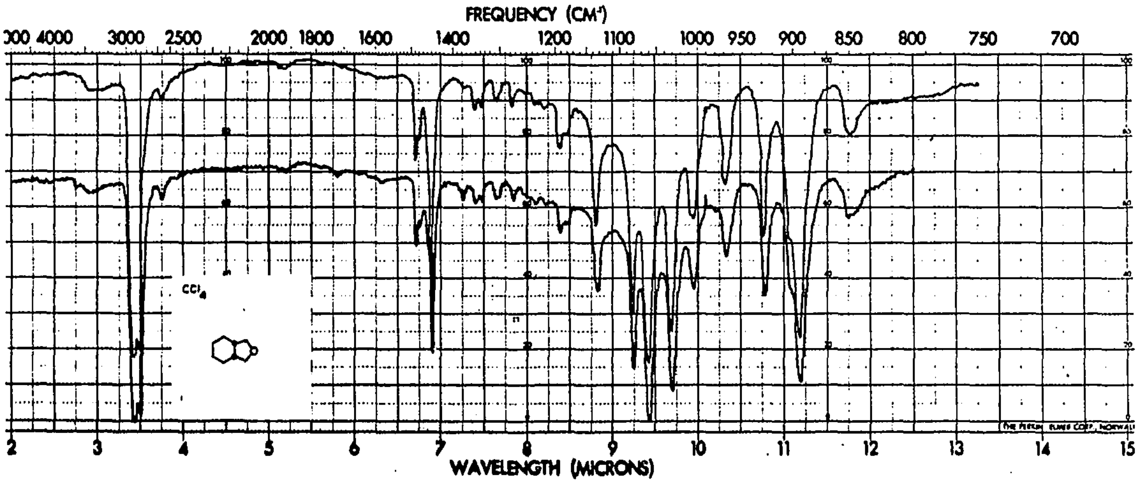
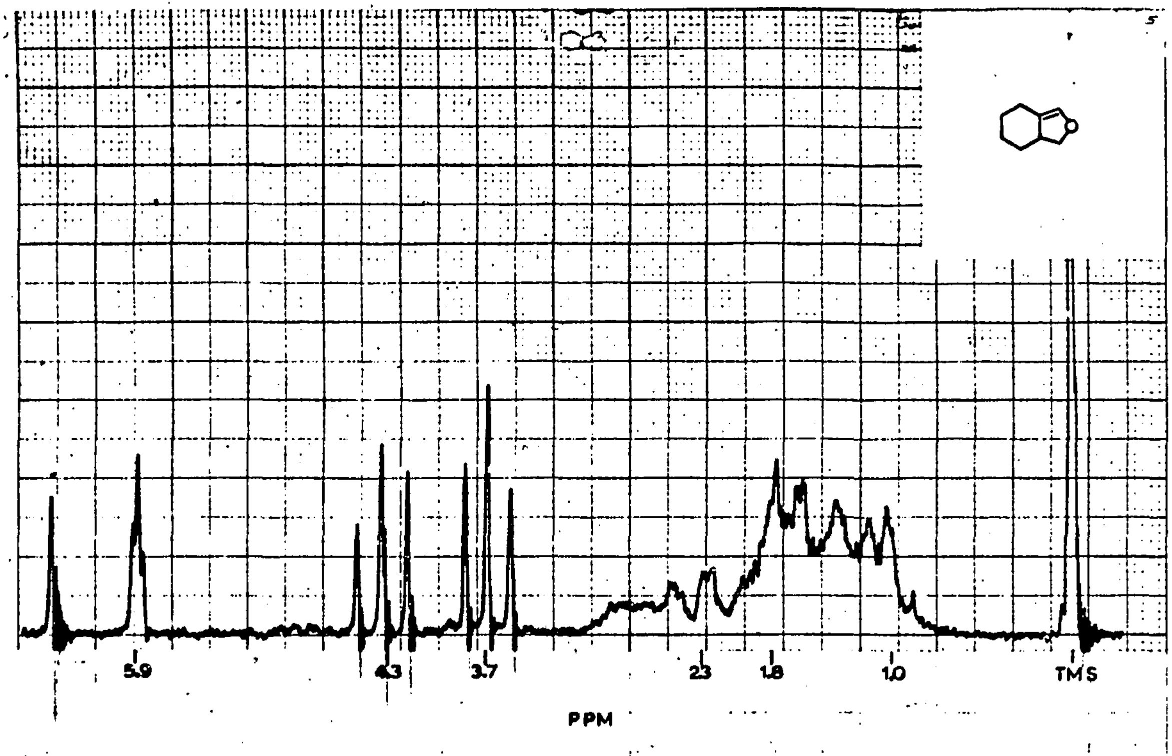
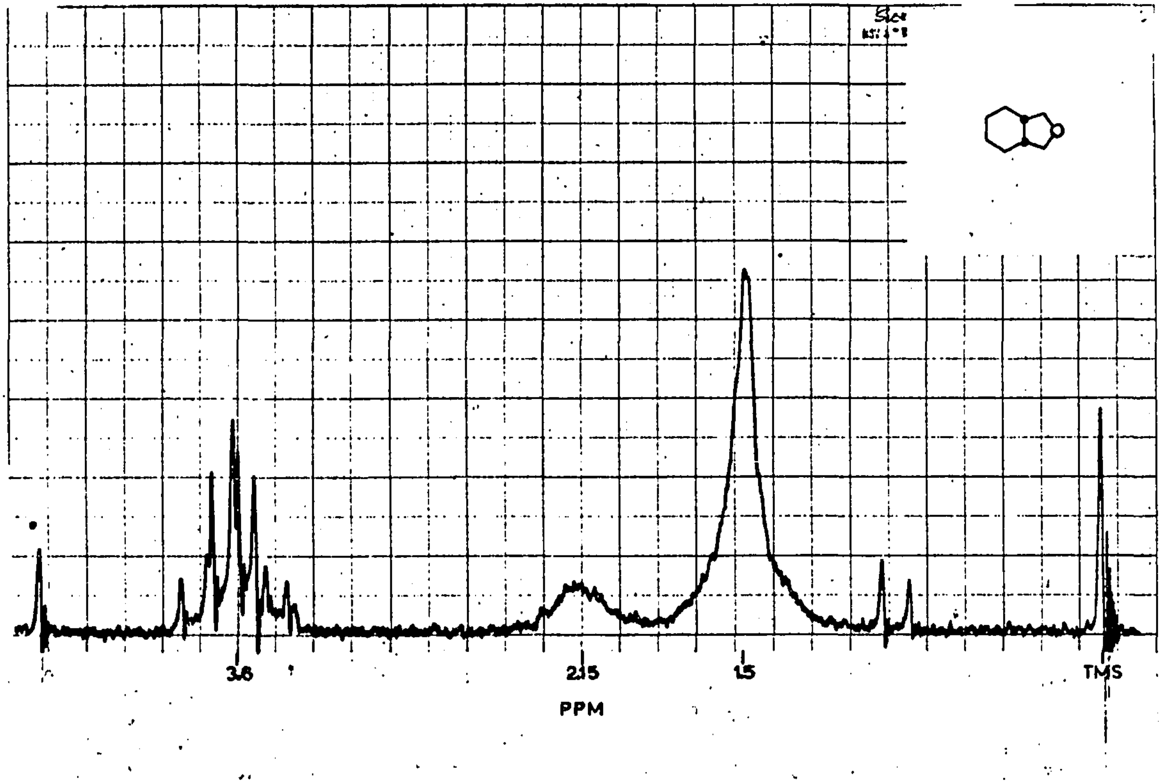

FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 9. Nuclear magnetic resonance spectra

Top - 3,4-Tetramethylene-2,3-dihydrofuran (L)

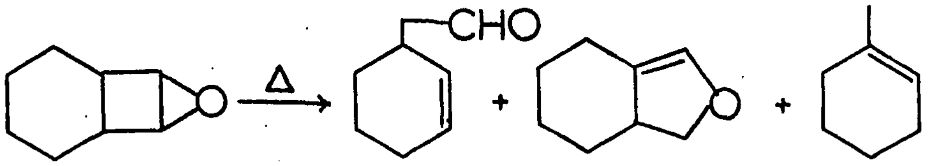
Bottom - 3,4-Tetramethylenetetrahydrofuran (XLIX)


5.9
4.3
3.7
2.3
1.8
1.0
TMS
PPM

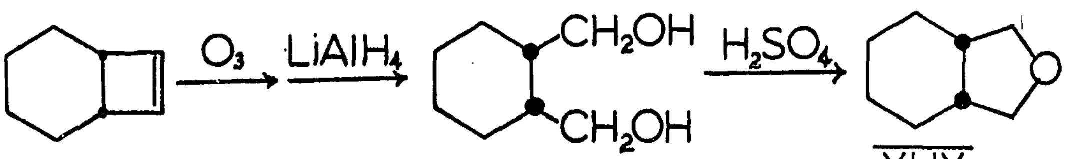

3.6
2.15
1.5
TMS
PPM

at 3.6 p.p.m. (Figure 9, p. 40). This suggested the more symmetrical 3,4-tetramethylenetetrahydrofuran (<u>cis</u> or <u>trans</u>) as the more likely structure for the dihydro enol ether.

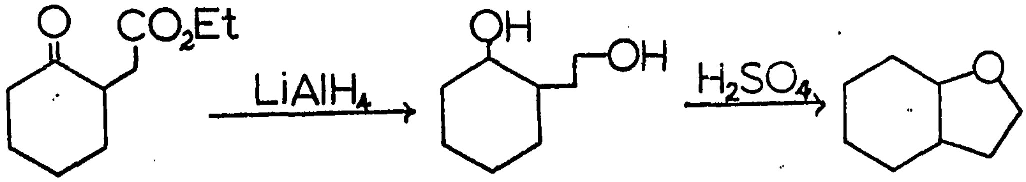
<u>Cis</u>-3,4-tetramethylenetetrahydrofuran (XLIX, <u>cis</u>-hexahydrophthalan) was synthesized from <u>cis</u>-bicyclo(4.2.0)oct-7-ene via ozonolysis, reduction to the diol and dehydration (40, 41, 42). The nuclear magnetic resonance spectrum of authentic XLIX was identical with that of the dihydro enol ether. The infrared spectra of the ethers were superimposable with absorption at 2930, 2860, 2670, 1590, 1480, 1450, 1135, 1082, 1060, 1030, 968, 926 and 892 cm^{-1} (Figure 8, p. 38). Thus the enol ether is 3,4-tetramethylene-2,3-dihydrofuran (L).



XIII XLVII L XLVI



XLIX



XLVIII

Various runs on the pyrolysis of bicyclo(4.2.0)oct-7-ene oxide gave the same products in the same ratio. Pyrolysis of this epoxide on a column of glass wool (greater surface area) gave the same results as pyrolysis on glass helices showing no surface effects. A similar lack of surface effects in epoxide pyrolyses has been reported (11).

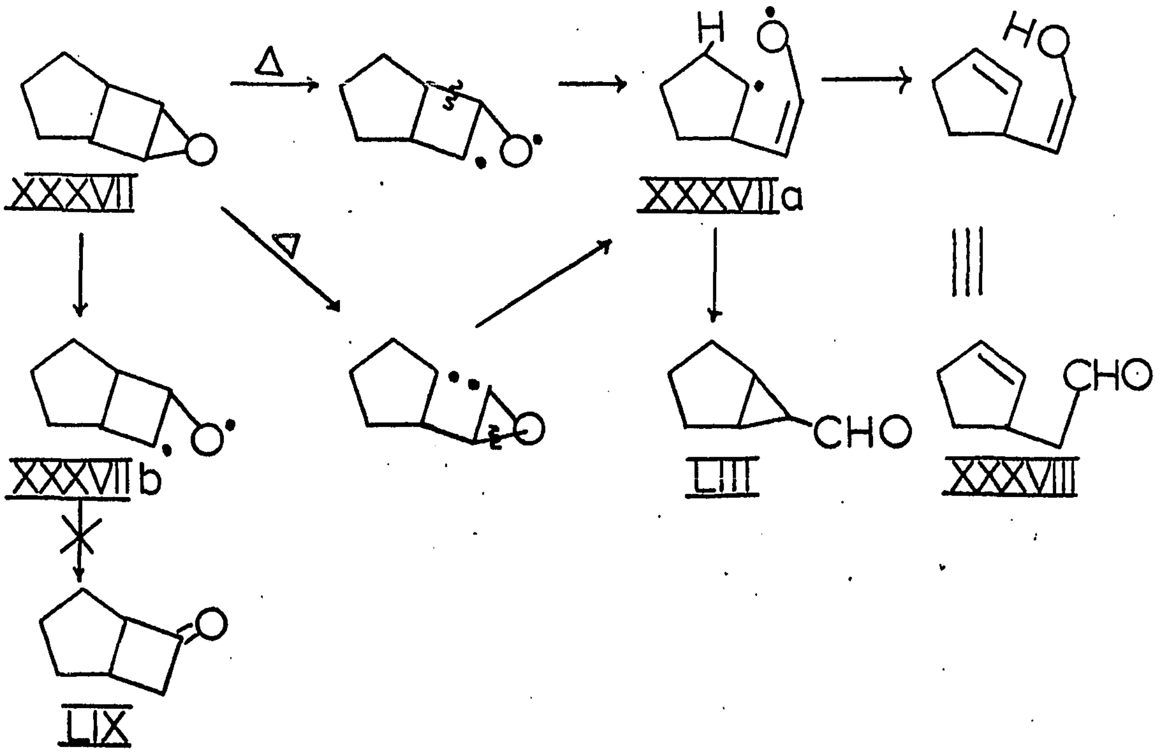
Pyrolysis of bicyclo(4.2.0)oct-7-ene oxide at lower temperature (350°) gives only 75% conversion with a smaller percentage of low boiling product. Pyrolysis at higher temperature (450°) gives less of the two major products, several low boiling products in higher yield and a slightly greater amount of a compound (LI) with a longer retention time on the gas chromatograph than the two major products, previously found in only trace amounts. Pyrolysis at 500° gives a higher yield of many low boiling products, almost none of the two major products obtained at 400°, several compounds of longer retention time on the gas chromatograph and much polymeric material.

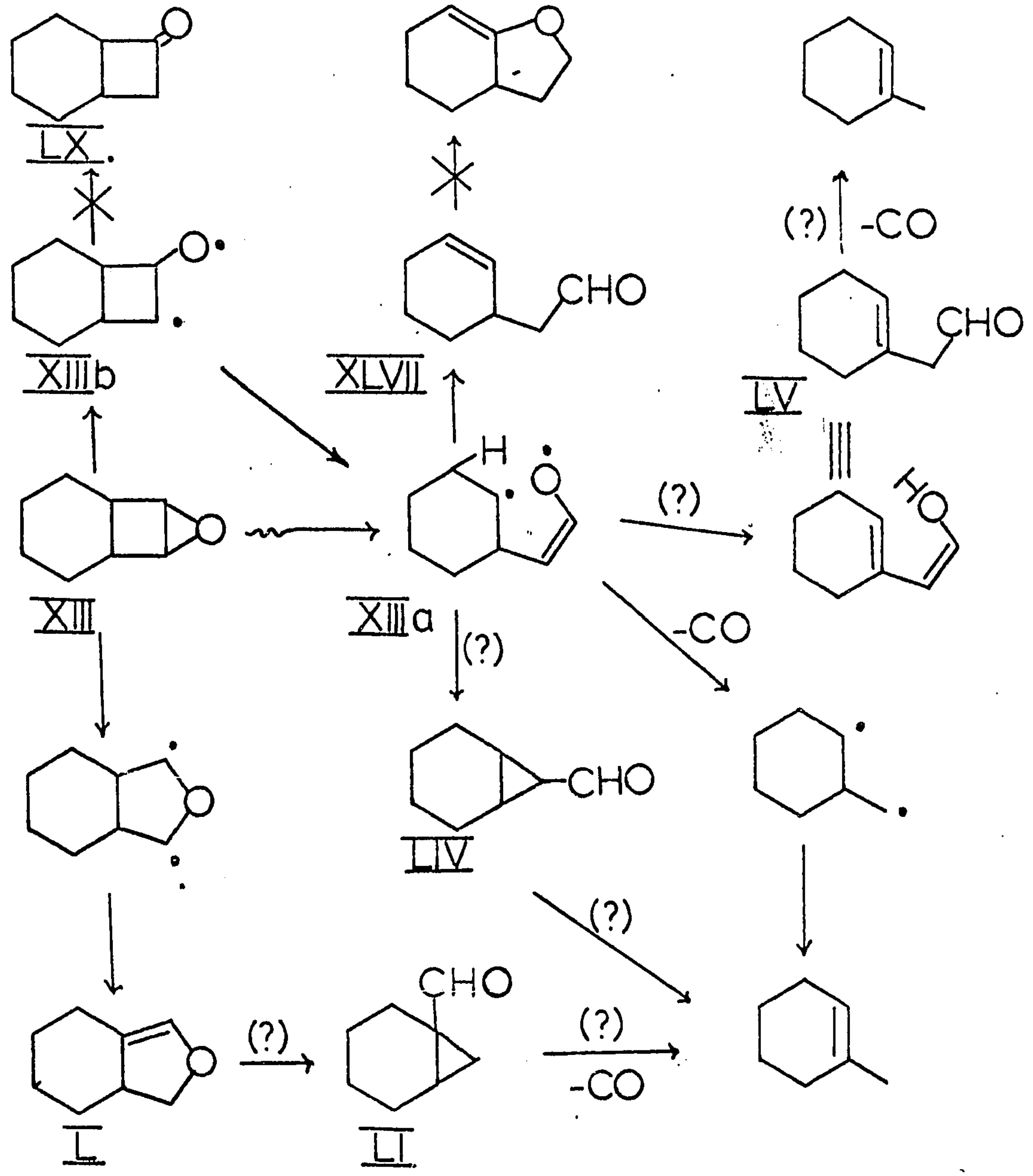
The trace compound (LI) was trapped from the gas chromatograph for spectral analysis. The infrared spectrum showed aldehydic hydrogen (2820 and 2740 cm^{-1}), carbonyl (1705 cm^{-1}) and cyclopropyl (3070, 3010 and 1035 cm^{-1}) absorption. The nuclear magnetic resonance spectrum showed an aldehydic proton at 8.47 p.p.m. (singlet), no olefinic protons and methylene proton absorption from 2 to 0.6 p.p.m. The compound may be bicyclo(4.1.0)heptane-1-carboxaldehyde (LI), possibly formed from the rearrangement of L. The formation of LI from L would be analogous to the formation of cyclopropanecarboxaldehyde in the pyrolytic rearrangement of 2,3-dihydrofuran (LII) (43). The large upfield shift of the aldehydic proton in the nuclear magnetic resonance spectrum is analogous to that of cyclopropanecarboxaldehyde which appears at 8.9 p.p.m.

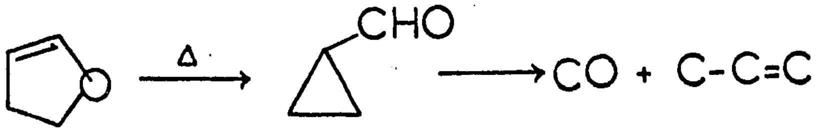
Schematically, it appeared reasonable that the rearrangements to the aldehydes had occurred via initial breaking of either the C-O epoxide bond followed by breakage of the appropriate C-C bond of the cyclobutane ring, or vice versa. On the flow sheet (p. 44), homolytic bond breakage is shown giving diradicals but the transformation could just as well be represented by heterolytic cleavage to give ionic species. It is now apparent that bond breakage is also occurring between the C-C epoxide bond of the cyclobutene oxide without C-O bond breakage followed by two 1,2-hydrogen shifts or a 1,3-hydrogen shift. The apparent lability of this bond has been previously demonstrated (17).

Considering the formation of bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde (LIII), one would expect the diradical intermediate (XXXVIIa) to close to the thermodynamically more stable *exo* isomer to the exclusion of the sterically hindered *endo* isomer.

The 1-methylcyclohexene could be produced by decarbonylation of the intermediate diradical (XIIIa), 7-norcarane carboxaldehyde (LIV), LI (via rearrangement from L), and Δ^1-cyclohexenylacetaldehyde (LV) (see p. 45). Cyclopropylcarboxaldehydes are known to decarbonylate upon heating to give ring opened products. Wilson reported that the pyrolysis of 2,3-dihydrofuran (LII) gave propene and carbon monoxide as the major products. The intermediate was shown to be cyclopropanecarboxaldehyde (43). Δ^1-Cyclohexenylacetaldehyde (LV) could decarbonylate through the aid of homoallylic conjugation of the β,γ-double bond which is not possible with the Δ^2-isomer (44). No Δ^1-cyclohexenylacetaldehyde was found in the pyrolysate from XIII.




LX
XIIIb
XLVII
CHO
(?)
-CO
LV
HO
H
XIII
XIIIa
(?)
-CO
CHO
LIV
(?)
L
LI
CHO
(?)
-CO

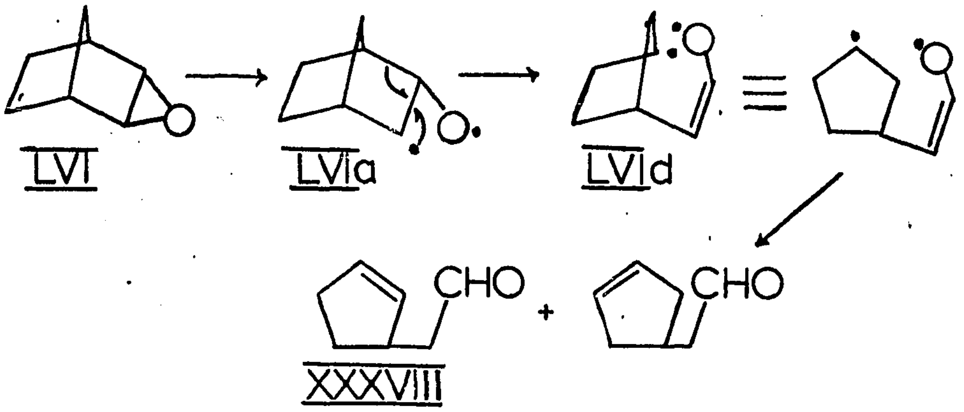

Δ
CHO
CO + C-C=C

The possibility of initial isomerization of the cyclobutene oxides to the corresponding cyclobutanones with further rearrangement to products was eliminated by experiment (see p. 57).

The possibility of rearrangement of the enol ether, L, to the bicyclic aldehyde, LI, and 1-methylcyclohexene was investigated. Pyrolysis of 0.20 g. of the enol ether, under reaction conditions identical to the pyrolysis of XIII (400°), gave 0.12 g. of material which was shown to be essentially unreacted enol ether by analysis by gas chromatography. There was a trace of low boiling material with a retention time equal to that of 1-methylcyclohexene and a trace of material corresponding to the bicyclic aldehyde. This material was again pyrolyzed at a higher temperature (420°) giving 0.06 g. of pyrolysate. This pyrolysate was essentially unreacted enol ether with a slightly greater amount of the two trace products. Therefore, it is unlikely that a majority of the 1-methylcyclohexene from the pyrolysis of XIII is coming from decomposition of the enol ether.

The Pyrolysis of Norbornene Oxide

If the enol diradical (XXXVIIa) was the intermediate in the pyrolysis of XXXVII, a similar diradical would be expected to give analogous results. It was therefore decided to pyrolyze norbornene oxide (LVI) which could theoretically give an analogous diradical (LVId) which could lead to Δ^2- or Δ^3-cyclopentenylacetaldehyde.



Norbornene oxide was prepared by peracid oxidation of norbornene and purified by sublimation. Vapor phase pyrolysis was effected by dropping the solid onto a column of glass helices in a temperature control oven and sweeping with a nitrogen stream. No pyrolysis was apparent under 500°. Complete conversion was effected at 550°.

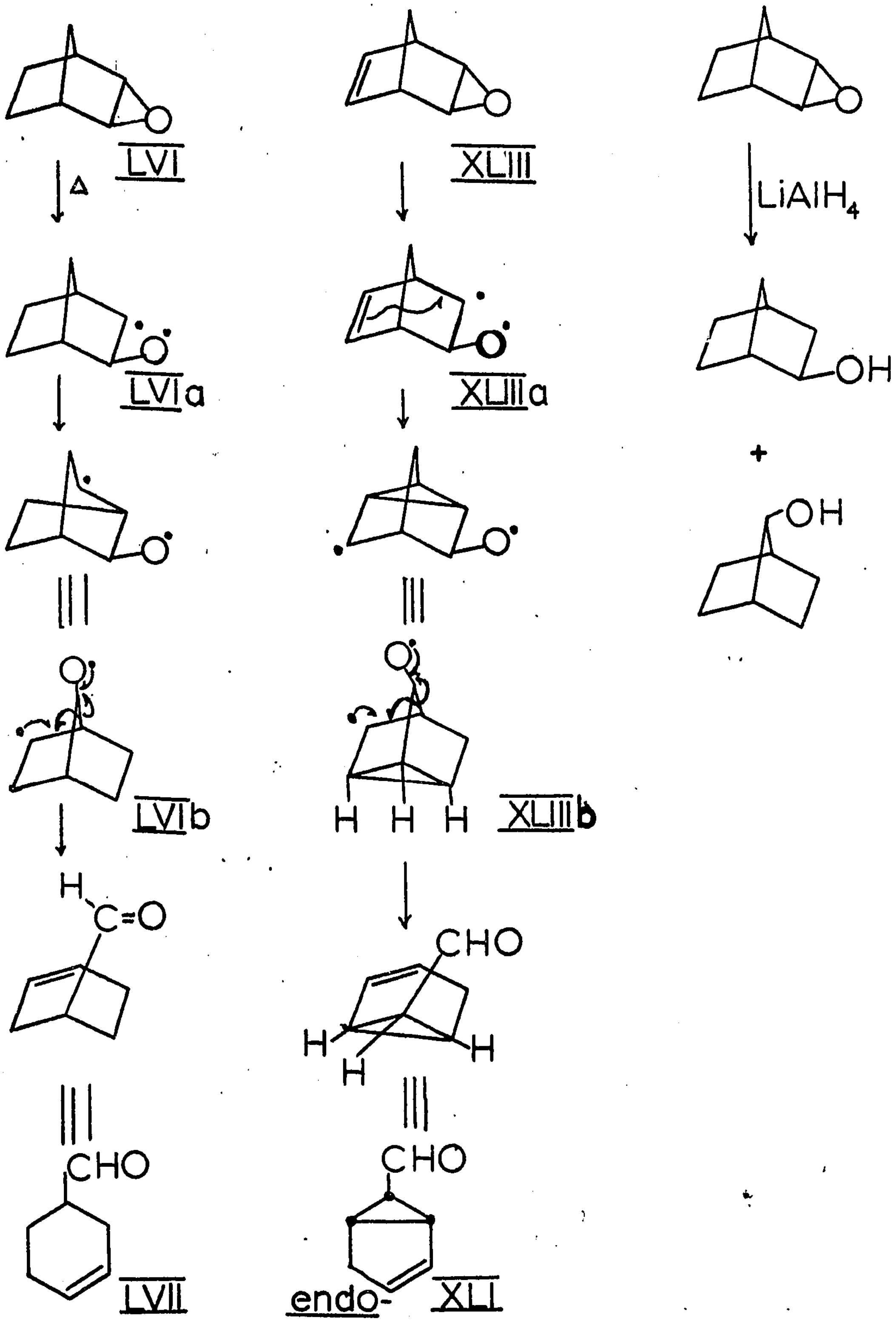
An infrared spectrum of the crude pyrolysate showed the presence of an aldehyde as well as several carbonyl bands. Analysis by gas chromatography on a Perkin-Elmer RX column showed three major peaks whose ratios varied slightly with each pyrolysis. Percentages were determined by integration of the peak areas on the chromatogram. Samples of these three products were collected from the gas chromatograph.

The major product of the pyrolysate (62-67%) was proven to be Δ^3-cyclohexenyl carboxaldehyde (LVII). The infrared spectrum was consistant for the unsaturated aldehyde with absorption at 3030, 2850, 2710, 1730, 1645 and 862 cm^{-1} (Figure 10, p. 54). The nuclear magnetic resonance spectrum showed one aldehyde proton as a singlet at 9.6 p.p.m., two olefinic protons at 5.6 p.p.m. appearing as a multiplet upon expansion, and integrated for ten total protons relative to two olefinic protons (Figure 11, p. 56). The coupling constants of aldehyde protons attached to cyclic moieties range from plus to minus and the protons occasionally appear as singlets instead of doublets. The 2,4-dinitrophenylhydrazone of the aldehyde had m.p. 176-7° (literature (45) m.p. 176-7°). The 2,4-dinitrophenylhydrazone of dihydro LVII had m.p. 171-2° (reported for the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde (46) m.p. 172°). An authentic sample of Δ^3-cyclohexenyl carboxaldehyde, synthesized by Diels-Alder addition of cyclobutadiene and acrolein, was supplied by Dr. Henry E. Hennis of the Dow Chemical Company, Midland, Michigan. The infrared sample of authentic material was superimposable with that of the aldehyde from the pyrolysate. The 2,4-dinitrophenylhydrazones of the aldehydes showed no mixed melting point depression.

The second recurring product from the pyrolysate (5-10%) sublimed in the collection tube. Its infrared spectrum showed a carbonyl absorption at 1745 cm^{-1} (Figure 10, p. 54). The nuclear magnetic resonance spectrum showed a complex eight proton methylene region from 1.3 to 2.0 p.p.m. and two protons shifted slightly downfield at 2.5 and 2.6 p.p.m., respectively. The ketone was shown to be norcamphor (XXX) by comparison of its infrared spectrum with that of the known compound purchased from the Aldrich Chemical Company. The 2,4-dinitrophenylhydrazone had m.p. 131-1.7° (literature (47) m.p. 130-1.5°).

The third identifiable product from the pyrolysate (5-10%) was an α,β-unsaturated ketone. The ultraviolet spectrum in 95% ethanol had λmax. 215 mμ (ϵ > 10,000). The infrared spectrum was consistent for Δ^2-cyclopentenone (LVIII) with absorption at 3050, 1716, 1645 and 1610 cm^{-1} (Figure 10, p. 54). The nuclear magnetic resonance spectrum was consistent with that reported for Δ^2-cyclopentenone (48) with one β-olefinic proton at 7.6 p.p.m., one α-olefinic proton at 6.1 p.p.m., two allylic methylene protons at 2.6 p.p.m. and two methylene protons <u>alpha</u> to a carbonyl at 2.2 p.p.m., all highly split (Figure 11, p. 56). The 2,4-dinitrophenylhydrazone of LVIII was deep red and had m.p. 165-6° (literature (49) m.p. 165-6°). No acetaldehydes were found in the pyrolysate.

The formation of LVII from norbornene oxide suggests a Wagner-Meerwein type shift (8) followed by further rearrangement (see p. 50). A similar rearrangement of the camphane radical has been reported by Berson, Olsen and Walia (50).


LVI
Δ
LVIa
LVIb
LVII
XLIII
XLIIIa
XLIIIb
endo-
XLI
LiAlH$_4$
OH
+
OH
H
C=O
CHO
H
H
H

An analogous intermediate (XLIIIb) to LVIb can be shown for the conversion of the monoepoxide of norbornadiene (XLIII) to XLI. By comparison, this rearrangement goes upon slight heating while the saturated epoxide requires extremely high temperatures. This is probably due to the ability of the double bond to stabilize the cleaved epoxide intermediate.

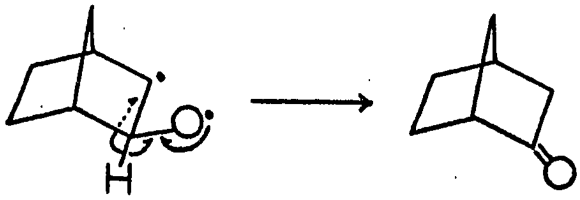
By analogy to the postulated intermediate, LVIb, the lithium aluminum hydride reduction of norbornene oxide (reported to be 94% *exo* and 6% *endo*) gives 7-norborneol as well as the expected 2-norborneol (*exo* isomer) (51).

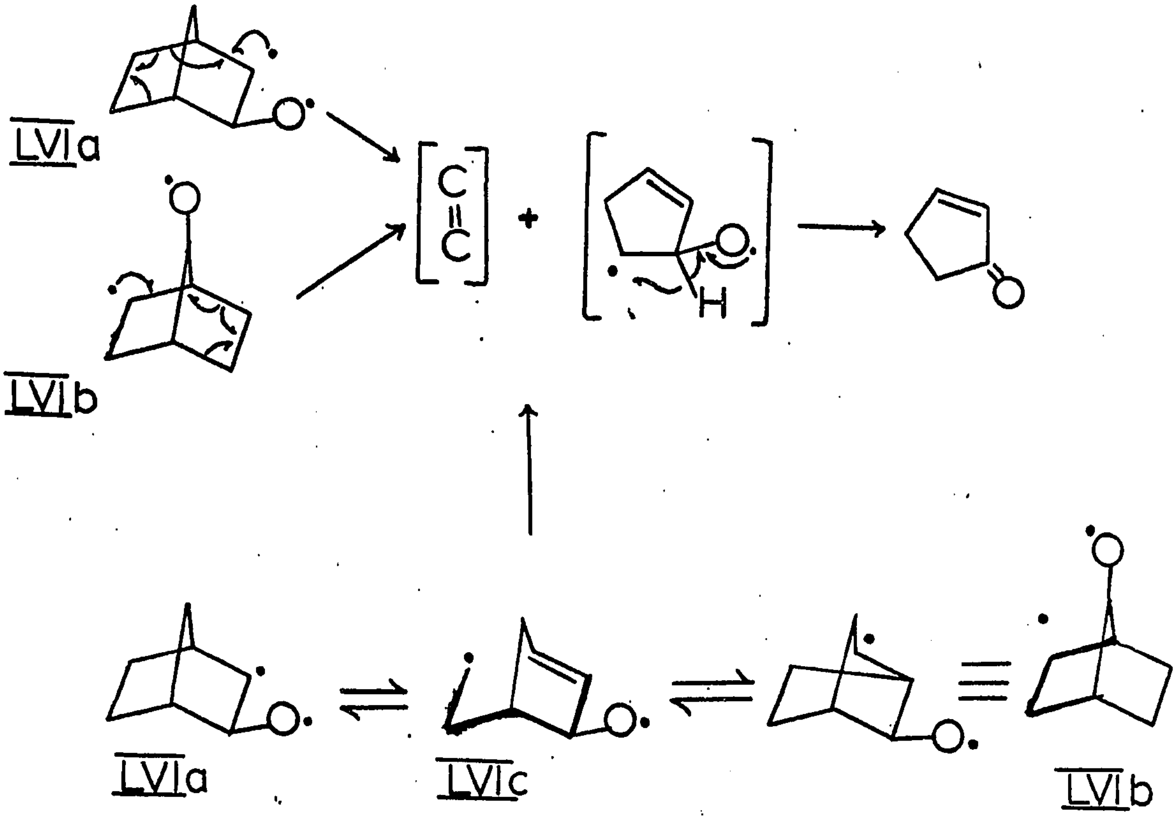
Norcamphor presumably arises via a 1,2-hydrogen shift which is common in epoxide pyrolysis (1). Similarly, reaction of norbornene oxide with magnesium halide is reported to give norcamphor as the major product (51).

The formation of Δ^2-cyclopentenone can be depicted as forming from the diradical intermediates, LVIa and LVIb, via elimination of ethylene followed by a 1,2-hydrogen shift (see p. 52).

The possibility of norcamphor being an intermediate in the formation of LVII and LVIII was ruled out by later experiments (see p. 57).

Another possible intermediate is LVIc which, by addition or elimination, could lead to the three products. This intermediate is analogous to that reported for the rearrangement of the camphane radical (XXXVa) (50).


H


LVI a
C
C
H
LVI b
LVI a
LVI c
LVI b

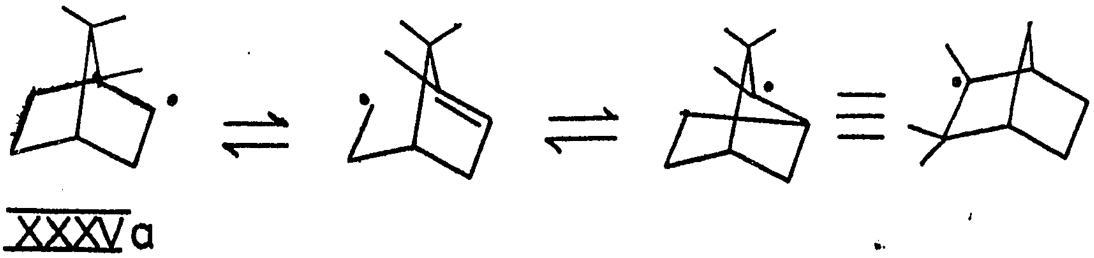
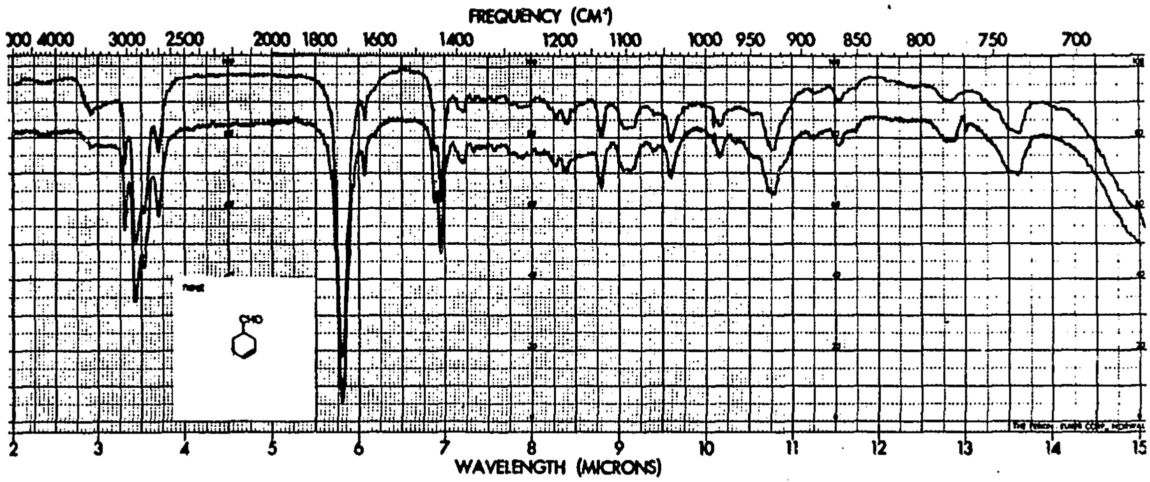

XXXV a

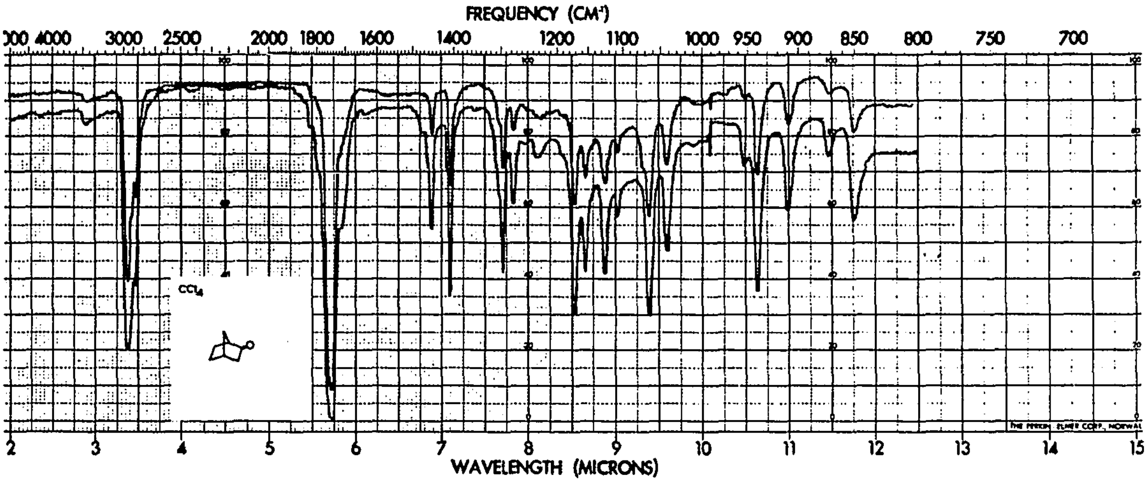
Figure 10. Infrared spectra

Top - Top, Δ^3-Cyclohexenylcarboxaldehyde (LVII)
Bottom, Authentic sample

Middle - Top, Norcamphor (XXX)
Bottom, Authentic sample

Bottom - Δ^2-Cyclopentenone (LVIII)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
NEAT
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
THE PERKIN-ELMER CORP., NORWALK


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl4
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
THE PERKIN-ELMER CORP., NORWALK

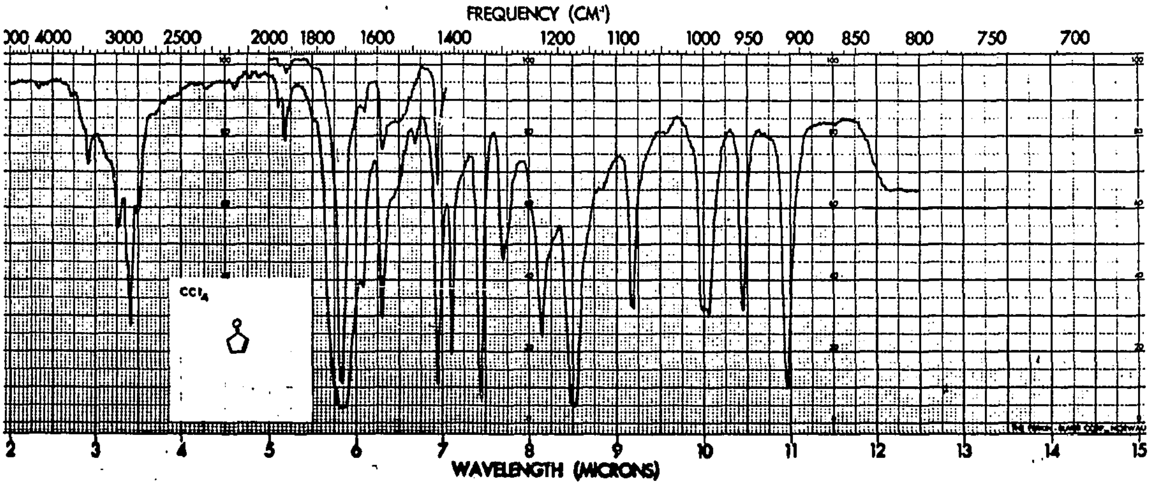
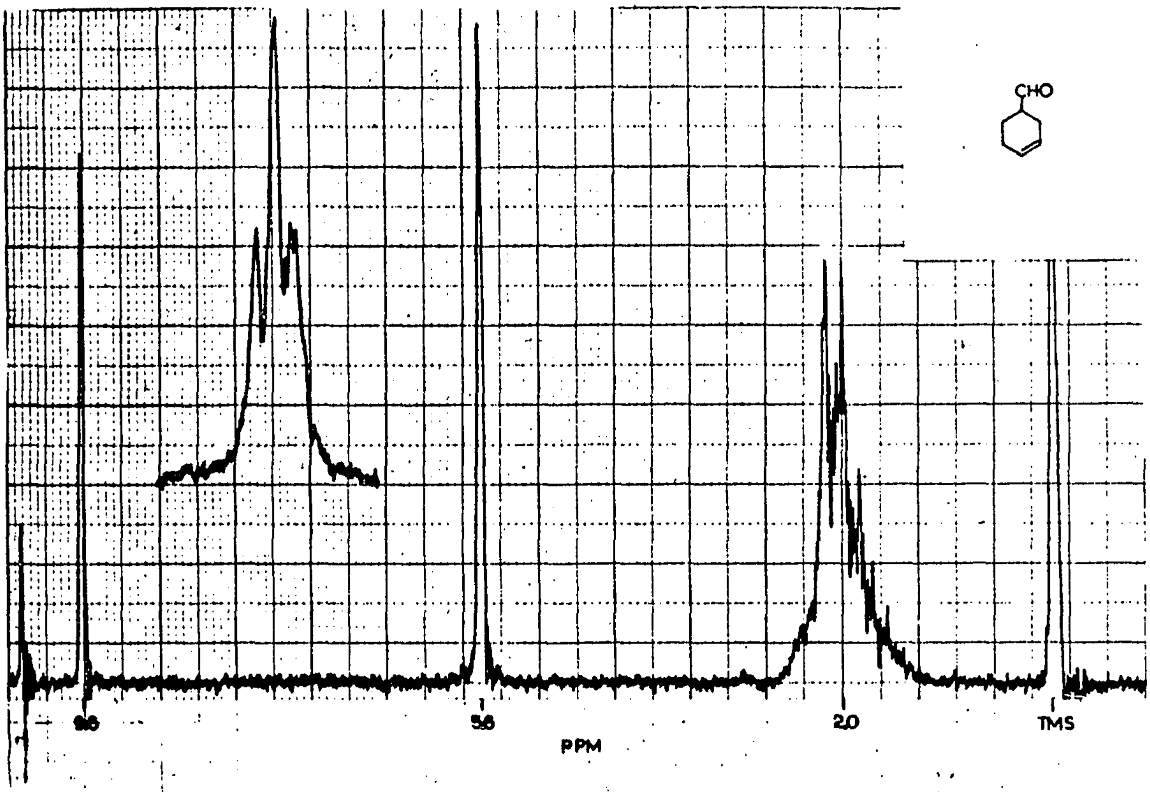
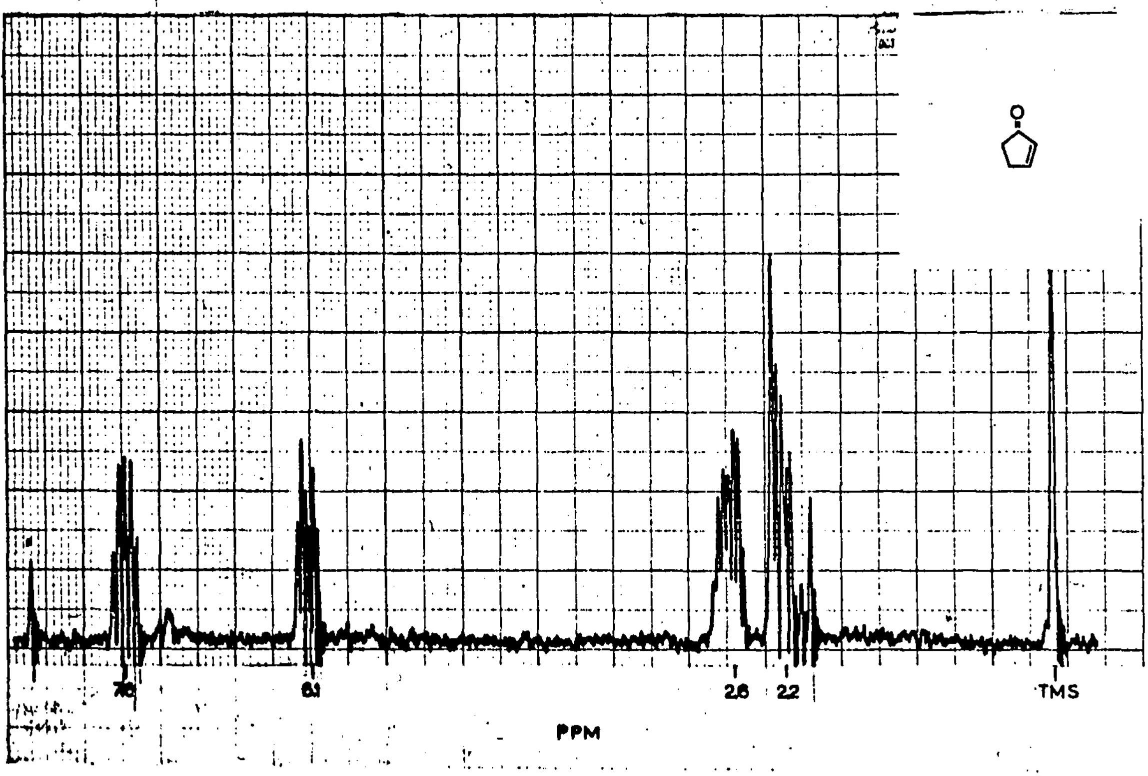

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl4
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
THE PERKIN-ELMER CORP., NORWALK

Figure 11. Nuclear magnetic resonance spectra

Top - Δ^3-Cyclohexenylcarboxaldehyde (LVII)
Bottom - Δ^2-Cyclopentenone (LVIII)


CHO
9.6
5.6
2.0
TMS
PPM


O
7.6
6.1
2.6
2.2
TMS
PPM

Pyrolysis of Cyclobutanones and Norcamphor

In the pyrolysis of the two cyclobutene oxides, XXXVII and XIII, two of the possible products were the corresponding ketones, bicyclo(3.2.0)heptan-6-one (LIX) and bicyclo(4.2.0)-octan-7-one (LX), which could be formed via a 1,2-hydrogen shift from the diradical intermediates, XXXVIIb and XIIIb. These compounds were not observed in the pyrolysate but it was possible that they had formed as intermediates and then decomposed, under the reaction conditions, to the products observed.

In the pyrolysis of norbornene oxide (LVI), the corresponding ketone, norcamphor, was observed as a minor product but could also have been the major intermediate in the reaction.

To test these possibilities, the ketones were subjected to pyrolysis under reaction conditions identical to those of the pyrolyses of the epoxides.

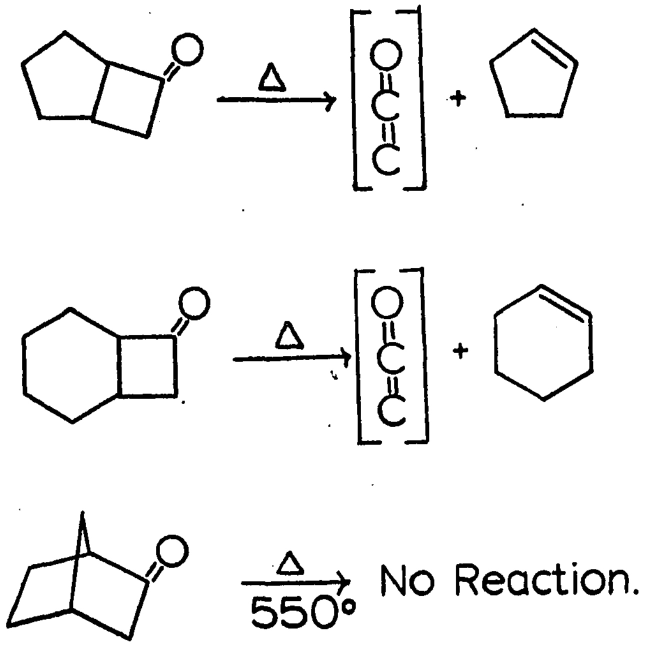
Bicyclo(3.2.0)heptan-6-one (LIX) was obtained from bicyclo(3.2.0)hept-6-ene by hydroboration (52) followed by chromic acid oxidation in ether via the procedure of Brown and Garg (53). The infrared spectrum showed carbonyl absorption at 1780 cm^{-1}. The semicarbazone of LIX had m.p. 200-1.5° (literature (54) m.p. 198.5-201°).

Pyrolysis was performed by the identical procedure and reaction conditions (420°) used in pyrolyzing the corresponding epoxide (XXXVII). The ketone completely decomposed to a gas and a low boiling liquid. Comparison of retention times on the gas chromatograph suggested the liquid to be cyclopentene. The infrared spectrum of the liquid was superimposable with that of known cyclopentene (1612 cm^{-1}). No higher boiling products were observed. Assuming the gas to be ketene, the decomposition is analogous to the pyrolysis of cyclobutanone (18).

Bicyclo(4.2.0)octan-7-one (LX) was prepared from bicyclo(4.2.0)oct-7-ene via the procedure of Brown and Garg (55). The infrared spectrum had carbonyl absorption at 1780 cm^{-1}. Pyrolysis in the manner described for XIII (400°) gave a gas and a low boiling liquid. Comparison of retention times on the gas chromatograph suggested the liquid to be the expected cyclohexene. Comparison of the infrared spectrum with that of the known compound verified this conclusion. No higher boiling products were observed.

The solid norcamphor (XXX) was purchased from the Aldrich Chemical Company and used without further purification. Pyrolysis was performed in a manner identical to that used to pyrolyze the solid norbornene oxide. At temperatures as high as 550° norcamphor passed through the pyrolysis tube unchanged and sublimed in the cold trap. An infrared spectrum of the trapped material was superimposable with that of starting material.

Thus the cyclobutanones (LIX and LX) and norcamphor can not be intermediates in the pyrolysis of the cyclobutene oxides (XXXVII and XIII) and norbornene oxide.



Photolysis of Cyclobutanones and Norcamphor

In order to synthesize the acetaldehydes (XXXVIII and XLVII) obtained from the pyrolysis of the cyclobutene oxides (XXXVII and XIII), the corresponding cyclobutanones (LIX and LX) were subjected to photolysis. It was hoped that α-cleavage of the cyclobutanone followed by intramolecular hydrogen abstraction would give the unsaturated aldehydes (20).

A 5% solution of bicyclo(3.2.0)heptan-6-one (LIX) in ether was placed in an internally water cooled Pyrex vessel and irradiated with a General Electric UA-3 mercury arc lamp for one day. Removal of ether left a gummy, polymeric material. The desired acetaldehyde (XXXVIII) was not apparent according to analysis by gas chromatography. The material was not analyzed further.

A 10% solution of bicyclo(4.2.0)octan-7-one (LX) in ether was irradiated in a similar fashion for four hours. Removal of ether left a polymeric residue. Analysis by gas chromatography showed that the desired acetaldehyde (XLVII) was not present. The material was not analyzed further.

In an attempt to synthesize Δ^2-cyclopentenylacetaldehyde (XXXVIII), a 10% solution of norcamphor (XXX) in n-butyl ether was placed in an internally water cooled Pyrex vessel and irradiated by an external mercury arc lamp. After several hours, an apparently clean conversion to a photoproduct was taking place as shown by analysis by gas chromatography on a Perkin-Elmer RX column. After several days, about 50% of the norcamphor had been converted. To speed up the process, the irradiation was conducted in a magnetically stirred, water cooled Pyrex immersion well apparatus with a quartz jacketed Hanovia immersion lamp. Using 10 g. of norcamphor in 100 ml. of 95% ethanol, the conversion was 50% complete in 9 hours. At the end of 24 hours, the conversion was almost quantitative. Injection of measured aliquot samples into the gas chromatograph showed that the final concentration of photoproduct was almost equal to the initial concentration of starting material. After removing the solvent in vacuo, distillation gave a 67% yield of photoproduct. Much polymer is formed in the distillation. The photoproduct was shown to be the expected Δ^2-cyclopentenylacetaldehyde (XXXVIII) by the chemical transformations outlined below.

The 2,4-dinitrophenylhydrazone of the aldehyde had m.p. 103-5° (literature (35) m.p. 98-9°). The semicarbazone of XXXVIII had m.p. 115-7° (literature (56) m.p. 116°).

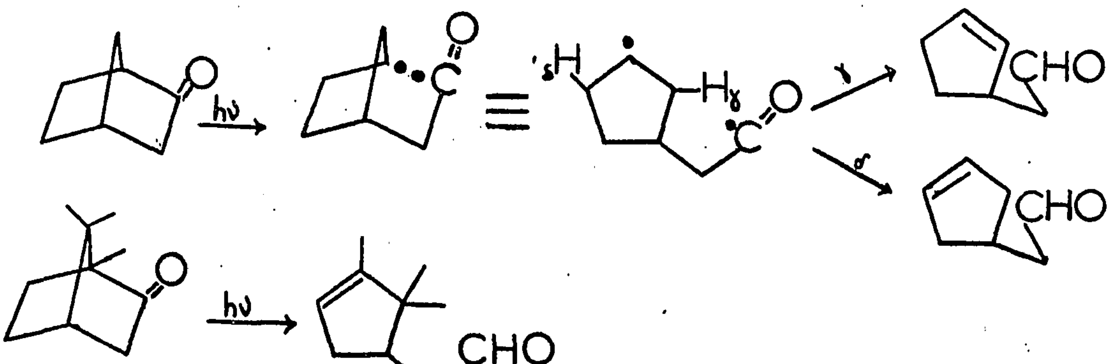
The aldehyde was oxidized to the corresponding carboxylic acid with silver oxide (57). The amide derivative of the carboxylic acid had m.p. 130-2° (reported for the amide derivative of Δ^2-cyclopentenylacetic acid (58) m.p. 131.5-2.5°). A mixed melting point with the amide derivative of authentic Δ^2-cyclopentenylacetic acid (XL), synthesized via the procedure of Noller and Adams (36), showed no depression. Cristol and Freeman reported that Δ^2-cyclopentenylacetamide has m.p. 131.5-2.5° and the Δ^3-isomer has m.p. 132.5-3.5° with no depression of the melting point when the two are mixed together. However, they reported differences in the infrared spectra (KBr) of these amides (58). The infrared spectrum of the amide obtained from the oxidized photoproduct was consistant with that reported for Δ^2-cyclopentenylacetamide (3360, 3190, 3060, 1660, 1630, 1353, 1320, 1300, 1280, 1235, 1205 and 1155 cm^{-1}.

The aldehyde was reduced to the corresponding alcohol with lithium aluminum hydride in ether. The α-naphthylurethan derivative had m.p. 82-3.5° and showed no mixed melting point depression on admixture with an authentic sample of the α-naphthylurethan of 2-(Δ^2-cyclopentenyl)ethanol.

The aldehyde was shown to be identical to the aldehyde obtained from the pyrolysis of bicyclo(3.2.0)hept-6-ene oxide by comparison of their infrared spectra (Figure 12, p. 64; and Figure 2, p. 20), nuclear magnetic resonance spectra and a mixed melting point determination of their 2,4-dinitrophenylhydrazones.

The preferred formation of the Δ^2-isomer over the Δ^3-isomer is readily predicted by examining models of the cleaved intermediate (XXXa). The protons <u>delta</u> to the carbonyl (leading to the Δ^3-isomer) are 50% further away from the carbonyl carbon than the <u>gamma</u> protons (leading to the Δ^2-isomer).

In the irradiation of camphor (XXXV), a Δ^3-cyclopentenylacetaldehyde is formed, but there are no <u>gamma</u> protons to abstract (59).



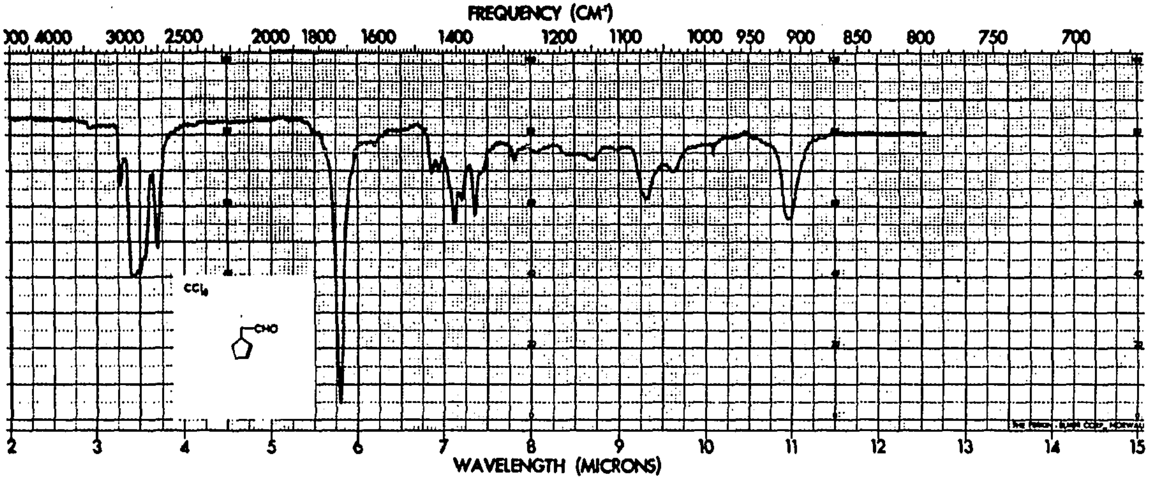
XXXV

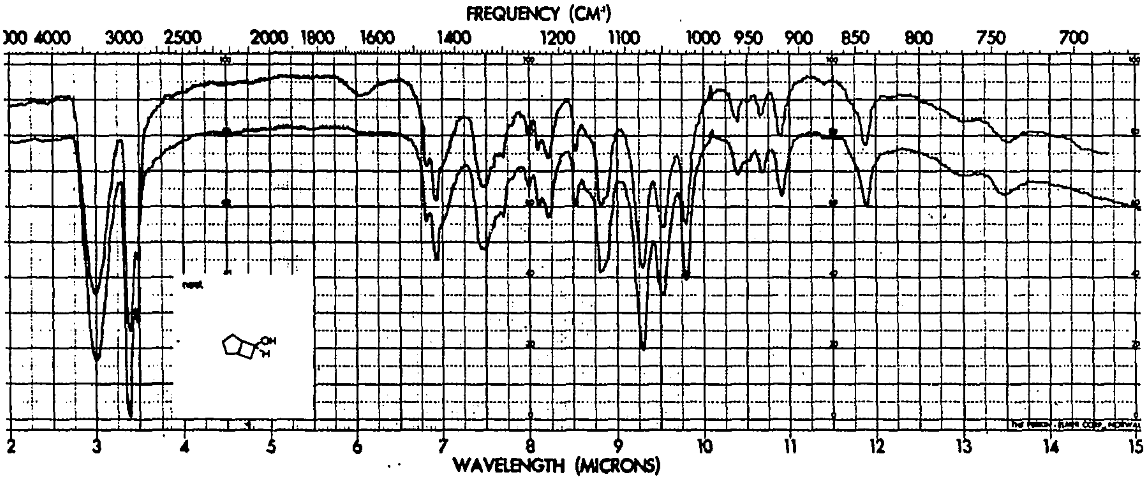
Figure 12. Infrared spectra

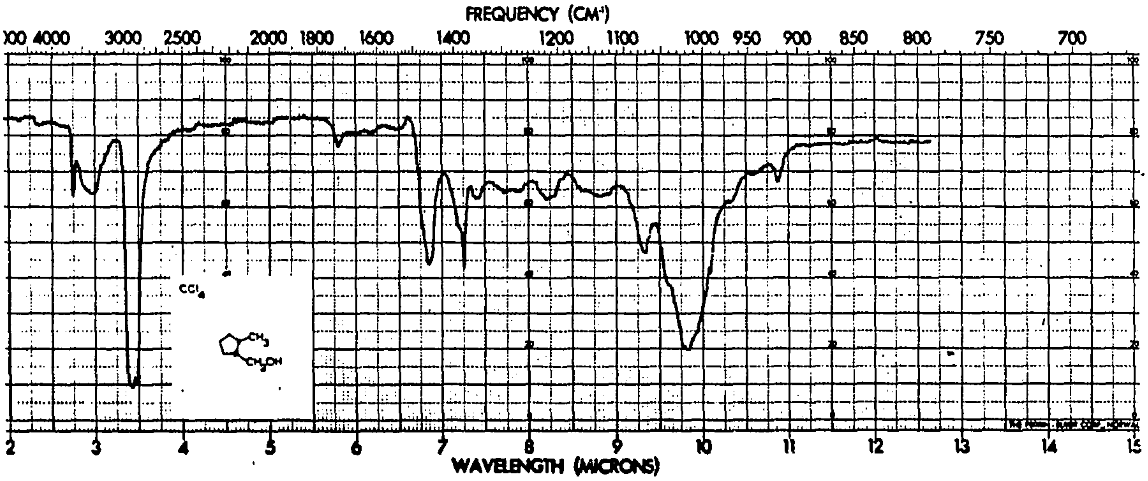
Top - Δ^2-Cyclopentenylacetaldehyde (XXXVIII) from photolysis of norcamphor

Middle - Top, Bicyclo(3.2.0)heptan-*exo*-6-ol (LXI)
Bottom, Authentic sample

Bottom - *Cis*-2-methylcyclopentanemethanol (LXII)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
neat
OH
H
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
CH₃
CH₂OH
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

The formation of a ketene, the competing product in α-cleavage, was not expected since it was shown that the irradiation of camphor apparently gave no ketene (22).

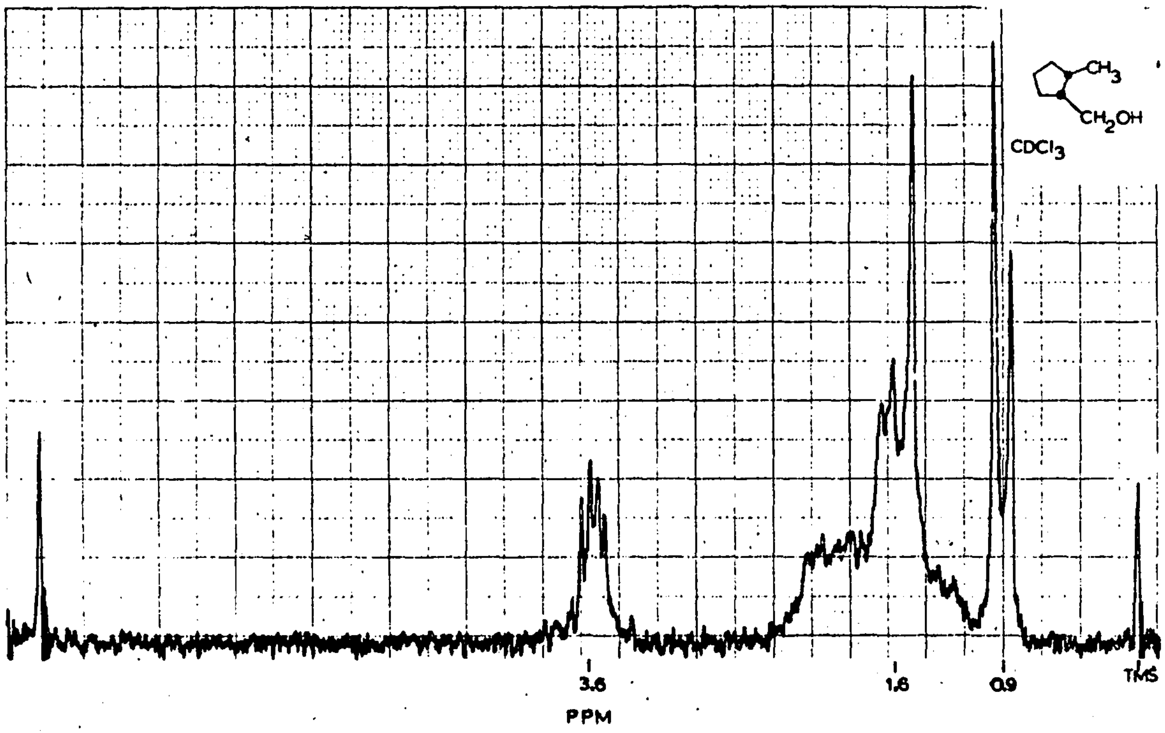
The Lithium Aluminum Hydride Rearrangement of Bicyclo(3.2.0)hept-6-ene Oxide

In order to prepare exo-bicyclo(3.2.0)heptan-6-ol (LXI), the epoxide, XXXVII (exo isomer), was reacted with lithium aluminum hydride in ether. Analysis by gas chromatography on a Perkin-Elmer RX column showed the presence of two alcohols from the reaction mixture. Samples were collected from the gas chromatograph for spectral analysis.

The major product (65%) was the expected exo alcohol (LXI), as shown by synthesis from bicyclo(3.2.0)hept-6-ene via hydroboration (52) and comparison of the infrared spectra of the two alcohols which were superimposable (Figure 12, p. 64). The nuclear magnetic resonance spectrum showed a two proton multiplet at 3.6 p.p.m., a methyl doublet ($J \sim 6$ c.p.s.) at 0.9 p.p.m., and integrated for fourteen total protons relative to two protons at 3.6 p.p.m. (Figure 13, p. 67). Therefore, the epoxide, XXXVII, had picked up four protons in reduction to the primary alcohol.

Prior to the completion of this study, Cope and Gleason reported obtaining cis-2-methylcyclohexanemethanol (XV) from the lithium aluminum hydride reduction of both exo and endo-bicyclo(4.2.0)oct-7-ene oxides (XIII and XIV) (17).

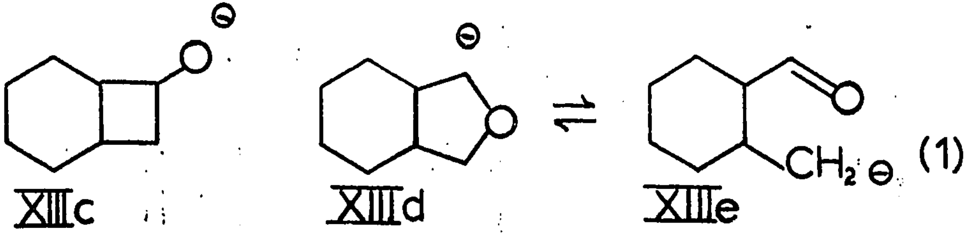
Figure 13. Nuclear magnetic resonance spectrum of *cis*-2-methylcyclopentanemethanol (LXII)


CH3
CH2OH
CDCl3
3.6
1.6
0.9
TMS
PPM

By analogy, and from our spectral data, we presumed our unexpected alcohol to be *cis*-2-methylcyclopentanemethanol (LXII). The α-naphthylurethan derivative of LXII had m.p. 91-2° (reported for the α-naphthylurethan of *cis*-2-methylcyclopentanemethanol (60) m.p. 92°; *trans* isomer (60) m.p. 98°).

Cope and Gleason showed that initial attack by hydride cannot lead to the same intermediate for both alcohols, eliminating XIIIc as a possible intermediate for the formation of XV. They also showed that either pure *exo* or *endo* epoxide (XIII, XIV) give the same results (17). To explain their results, they suggest attack at the C-C bond of the oxide ring forming a carbanion (XIIId), which could be considered a tautomeric form of XIIIe, which further reduces to product. This same C-C bond has been shown to be heat labile (see p. 43).

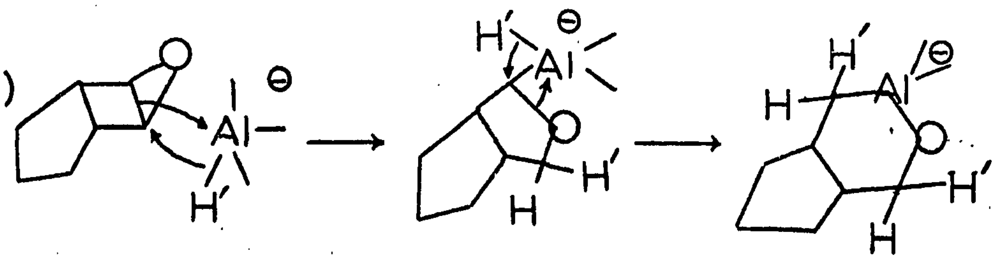
This suggested mechanism infers the formation of a carbon-aluminum bond. It was decided to determine if this mechanism was indeed possible or whether some different mechanism was involved (i.e., Lewis acid-catalyzed rearrangement prior to reduction).

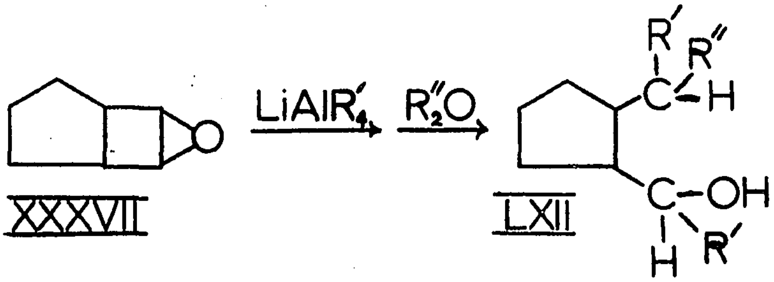


Nuclear magnetic resonance offered a simple and convenient method of investigation. Samples of the epoxide (XXXVII) were reduced with both lithium aluminum hydride and lithium aluminum deuteride (95%) and worked up with both water and deuterium oxide. Since deuterium atoms do not appear in the proton magnetic resonance spectrum, their positions of incorporation were marked by peaks diminished in area from the undeuterated alcohols. Integration of peak areas gave the relative amounts of deuterium incorporated. The alcohols (LXII) were isolated by separation and collection from the gas chromatograph utilizing a THEED column. Deuterium content was analyzed by integration of the methyl and hydroxymethylene peaks (both conveniently separated from the rest of the spectrum) relative to each other and to the total number of protons. The relative ratio of peak areas are listed as well as the relative number of protons based on the assumed total number of protons (see Table 1, p. 70). The results are in accord with the suggested mechanism of Cope and Gleason (mechanism 1). Other mechanisms will also fit this data, i.e. mechanism 2.

The organo-aluminum complex, XXXVIIc, is analogous to that suggested by Franzus and Snyder in their study of solvent effects on lithium aluminum hydride reductions of norbornadienes (61).

(2)





#1 R′, R″ = H #3 R′ = D, R″ = H

#2 R′ = H, R″ = D #4 R′, R″ = D

Table 1. Integrated peak areas and relative number of protons (based on the assumed total number of protons) from the nuclear magnetic resonance spectra of cis-2-methylcyclopentanemethanol (LXII) and deuterated LXII

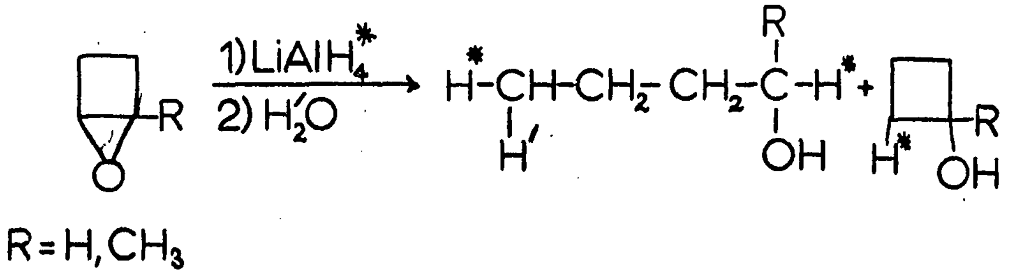
Flask	Integrated peak areas CH_3	$C\underline{H}_2$-OH	total	Relative number of protons CH_3	$C\underline{H}_2$-OH	total
1	22	15	107	2.9	2.0	14.0
2	15	14	95	2.1	1.9	13.0
3	19	18[a]	102	2.2	2.1[a]	12.0
4	11	9	101	1.2	1.0	11.0

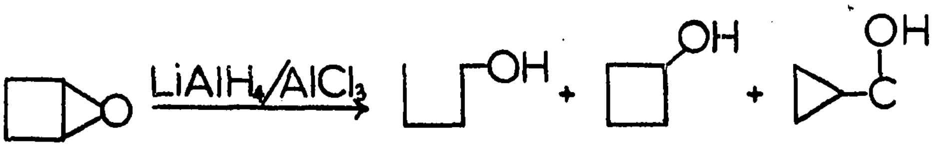
[a] Uncorrected for hydroxyl proton contained in peak.

At present, it is impossible to differentiate mechanisms (1) and (2) but it is clear that cleavage of the C-C bond of the epoxide and formation of a carbon-aluminum bond do occur. It remains to be seen whether these processes will be important in less strained systems.

After this work was initiated, Moore and Beede presented a talk at the 144th American Chemical Society Meetings on the lithium aluminum hydride reduction of cyclobutene oxides (62). From the abstracts of that talk, it appears their work is analogous to ours. Using deuterium labels, they traced the incorporation of hydrogen into the molecule. Their results and conclusions are in agreement with those presented above.

By adding aluminum chloride to the reaction mixture and varying the hydride/chloride ratio, Moore and Beede were able to vary the product mixture (62).





The Lewis Acid-Catalyzed Rearrangement of Cyclobutene Oxides

Moore and Beede recently reported the rearrangement of cyclobutene oxide (LXIII) and 1-methylcyclobutene oxide (LXIV) to cyclopropyl compounds by reaction with various Lewis acids (62). Thus LXIII with lithium iodide or aluminum chloride in ether rearranges very quickly and quantitatively to cyclopropylcarboxaldehyde (LXV). The substituted epoxide (LXIV) gives mainly cyclopropyl methyl ketone (LXVI) and some 1-methylcyclopropylcarboxaldehyde (LXVII) when reacted with lithium iodide. The stereochemical course of the rearrangement was not investigated.

In an effort to determine whether this rearrangement was stereospecific, it was decided to attempt isomerization of the cyclobutene oxides in our possession (XXXVII and XIII). By analogy, they should rearrange to the corresponding cyclopropylcarboxaldehydes which could then be oxidized to the corresponding carboxylic acids for identification. The exo and endo isomers of both bicyclo(3.1.0)hexane-6-carboxylic acid and bicyclo(4.1.0)heptane-7-carboxylic acid have been characterized. If the rearrangement was stereospecific, we expected to obtain one isomer; if not, then a mixture of isomers.

The reaction of both XXXVII and XIII with aluminum chloride or boron trifluoride etherate in ether gave no isomerization.

Anhydrous lithium iodide in ether was prepared by reacting lithium hydride with iodine in ether via the procedure of Taylor and Grant (63). Refluxing XIII with lithium iodide in ether gave rearrangement with much decomposition. Analysis by gas chromatography on a Perkin-Elmer RX column showed that two new compounds had formed in small amounts. Samples were collected from the gas chromatograph for spectral analysis.

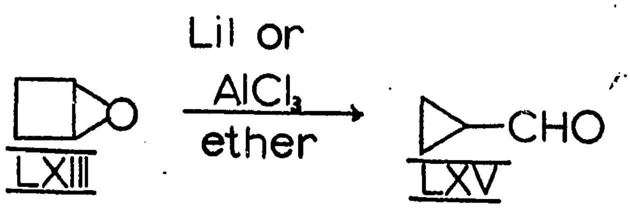
One of the products was shown to be Δ^2-cyclohexenylacetaldehyde (XLVII) by comparison of the infrared spectrum with that of the known compound obtained from the pyrolysis of XIII.

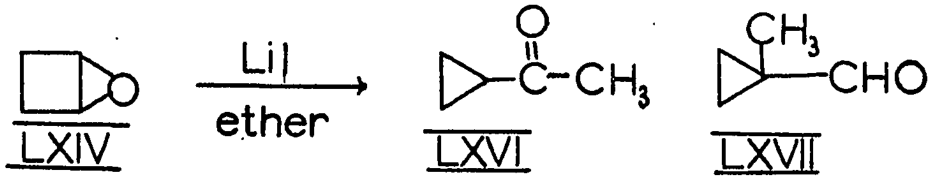
The second product was a saturated aldehyde. The infrared spectrum had absorption at 2860, 2700 (aldehyde), 1705 (carbonyl), 3010, 1020, 1000 and 858 cm^{-1} (cyclopropyl) (Figure 14, p. 77). The nuclear magnetic resonance spectrum showed an aldehyde doublet (J~4 c.p.s.) at 9.1 p.p.m., no olefinic protons, and a complex methylene region from 2.4 to 0.8 p.p.m.

The reaction mixture was chromatographed by towering on silica gel with benzene as solvent. About 0.2 g. (40%) of a colorless, viscous liquid was obtained. This was oxidized with silver oxide to a gummy product. Crystallization from ether gave a white solid which had m.p. 79-80°. The reported m.p. for bicyclo(4.1.0)heptan-endo-7-carboxylic acid (LXVIII, endo-7-norcarane carboxylic acid) is 79-80°, whereas the exo isomer is reported to melt at 96° (64). A mixed melting point determination with an authentic sample of LXVIII (kindly supplied by Professor J. A. Berson) had no depression. The infrared spectrum of the acid was superimposable with that of authentic LXVIII with carbonyl absorption at 1695 cm^{-1} and cyclopropyl hydrogen absorption at 3010 and 863 cm^{-1} (Figure 14, p. 77).

Considering the fact that the starting epoxide (XIII) is reported to be 87% of the exo isomer (17), this would suggest that the rearrangement to bicyclo(4.1.0)heptan-endo-7-carboxaldehyde (LIV) had taken place stereospecifically with inversion of configuration at the migration terminus.

As this manuscript was being prepared, other work was reported that verifies our findings, namely that $2\beta,3\beta$-epoxy-5α-cholestane (LXIX) rearranges upon reaction with methyl magnesium iodide to give a stereospecifically ring contracted product with inversion at the migration terminus (65). The authors suggest a Lewis acid-catalyzed rearrangement to both the cyclopentylcarboxaldehyde (LXX) and the cyclohexanone (LXXI) followed by reduction, via normal Grignard attack, to the products.


LiI or
AlCl$_3$
ether
CHO
LXIII
LXV


LiI
ether
O
C
CH$_3$
CH$_3$
CHO
LXIV
LXVI
LXVII

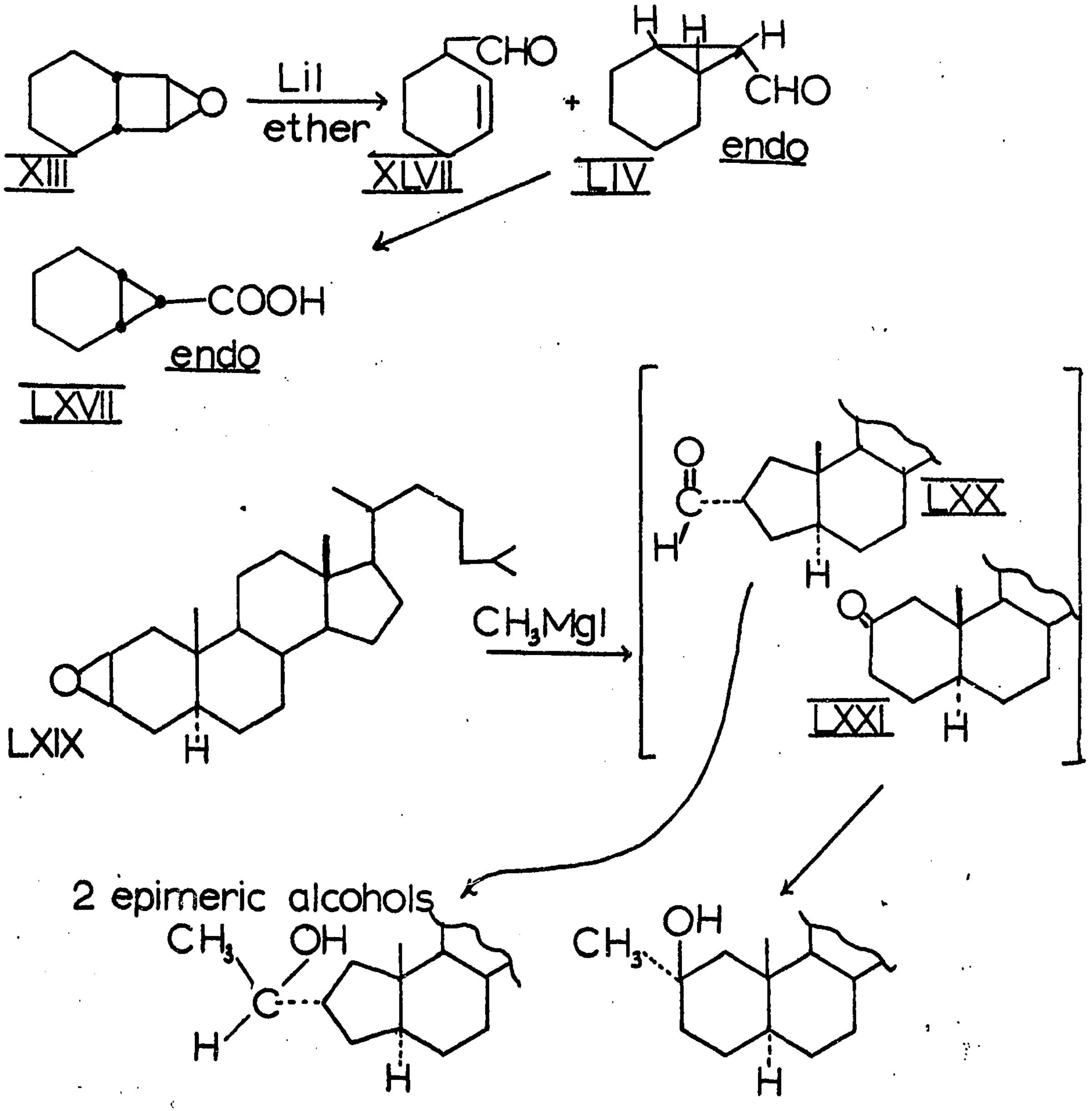
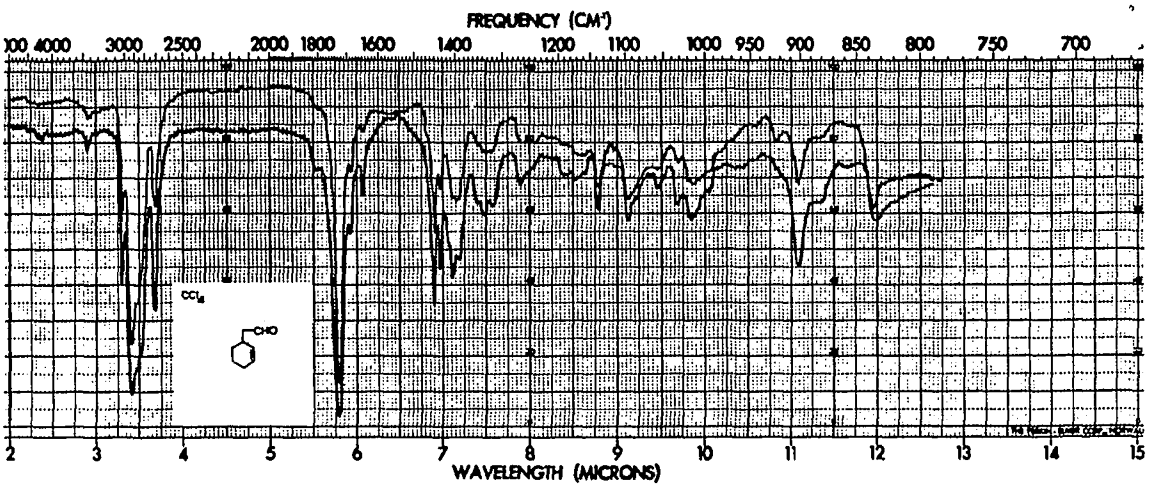

LiI
ether
CHO
+
H
H
H
CHO
endo
XIII
XLVII
LIV
COOH
endo
LXVII
CH$_3$MgI
O
C
H
H
LXX
O
LXXI
H
LXIX
H
2 epimeric alcohols
CH$_3$
OH
C
H
H
CH$_3$
OH
H

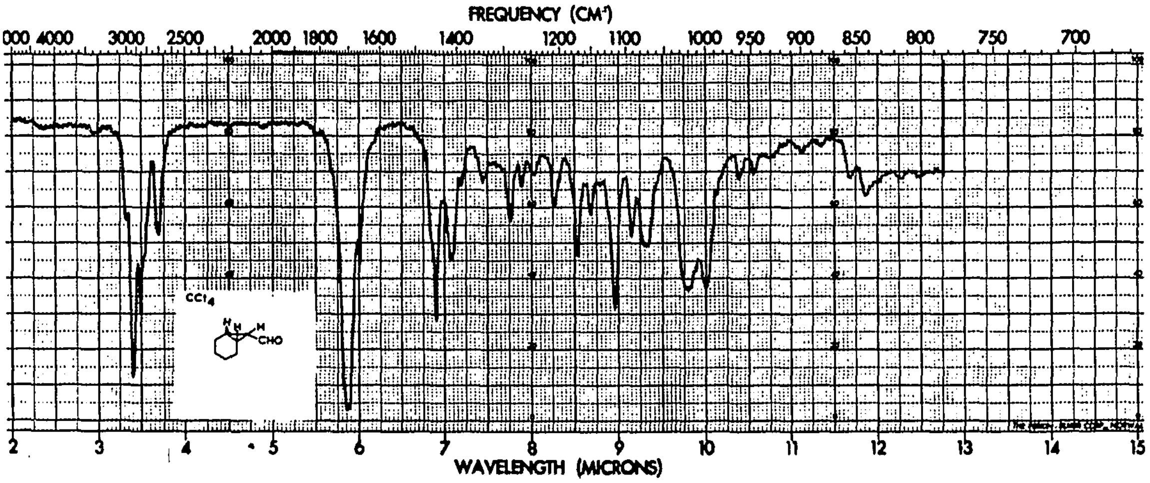
Figure 14. Infrared spectra

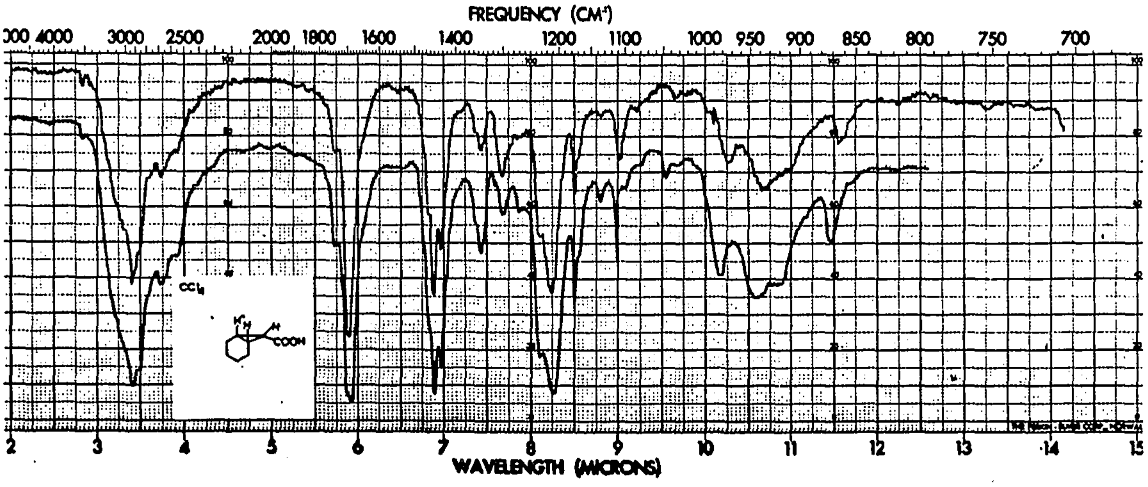
Top - Top, Δ^2-Cyclohexenylacetaldehyde (XLVII) from the pyrolysis of XIII
Bottom, Δ^2-Cyclohexenylacetaldehyde from the rearrangement of XIII with LiI

Middle - Bicyclo(4.1.0)heptan-*endo*-7-carboxaldehyde (LIV)

Bottom - Top, Bicyclo(4.1.0)heptan-*endo*-7-carboxylic acid (LXVIII, *endo*-7-norcarane carboxylic acid)
Bottom, Authentic sample


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
H
H
H
CHO
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700
CCl₄
H
H
H
COOH
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

EXPERIMENTAL

Experimental for the Pyrolysis of the Cyclobutene Oxides, Norbornene Oxide, the Cyclobutanones and Norcamphor

Bicyclo(3.2.0)hept-6-ene oxide (XXXVII)

Bicyclo(3.2.0)hept-6-ene (5.3 g., 0.056 mole) in chloroform (50 ml.) was added dropwise with stirring at 0° to a perbenzoic acid solution (7.8 g., 0.056 mole, determined by thiosulfate titration for active oxygen, in 100 ml. of chloroform). The reaction mixture was left to run until no peracid remained (10 hrs.). The chloroform solution was washed with 5% aqueous sodium bicarbonate until the water layer no longer precipitated benzoic acid upon acidification with 2N hydrochloric acid. The chloroform layer was washed twice with water (50 ml.) and dried over anhydrous magnesium sulfate. The solvent was removed with a rotary film evaporator, and the residue distilled under aspirator pressure to give a colorless liquid material (4.0 g., b.p. 72-5°/15 mm., infrared (neat): 3050, 950, 837 and 788 cm^{-1}, Figure 2, p. 20). Analysis by gas chromatography on a Perkin-Elmer RX column showed one peak.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.35; H, 9.34.

Bicyclo(4.2.0)oct-7-ene oxide (XIII)

Following the epoxidation procedure of Korach, Nielsen and Rideout (66), bicyclo(4.2.0)oct-7-ene (8.3 g., 0.077 mole), methylene chloride (65 ml.), and anhydrous sodium carbonate (20 g., 0.188 mole) were stirred together in a 250 ml. flask equipped with a thermometer and dropping funnel. To this was added 18 g. of 40% peracetic acid solution (0.095 mole) over ½ hr. maintaining the temperature at 20°. The reaction mixture was allowed to stir for two hrs., then filtered and the filter cake washed with methylene chloride. The solvent was removed from the filtrate with a rotary film evaporator. The residue was fractionally distilled under vacuum giving 4.1 g. (43%) of bicyclo(4.2.0)oct-7-ene oxide, b.p. 71-3°/16 mm. (reported (17) b.p. 82-4.5°/26 mm.), infrared (neat): 3040, 942, 825, 809 and 760 cm^{-1}; Figure 6, p. 34.

Pyrolysis of liquid epoxides and ketones

The liquid epoxide or ketone (1.0 g.) was drawn into a long needle syringe. The needle was then inserted through a septum at the top of a pyrolysis column. Twelve inches of the column were filled with 1/8" glass helices and encased in an oven maintained at 420° for XXXVII and LIX and 400° for XIII and LX (determined to be the optimum temperature for complete conversion of the epoxides and lowest number of products by gas chromatography). The temperature was determined by attaching an iron-constantan thermocouple to the column and to a Rubicon Potentiometer with reference temperature at 0°. The epoxide or ketone was allowed to drip onto the column at a slow enough rate to prevent flooding (10-15 drops/minute). The system was kept under a positive nitrogen pressure. The pyrolysate was trapped in a receiver kept at -70° (Dry Ice-acetone). Pyrolysate mixtures were separated by gas chromatography utilizing a Perkin-Elmer RX column at 75-150°. The products were collected from the gas chromatograph using 25-50 injections under the above conditions, in coiled glass tube receivers in a Dry Ice-acetone bath.

Δ^2-Cyclopentenylacetaldehyde (XXXVIII)

The major product from the pyrolysis of bicyclo(3.2.0)-hept-6-ene oxide was Δ^2-cyclopentenylacetaldehyde, infrared (CCl_4): 3080, 2820, 2720, 1725, 1615 and 910 cm^{-1}; Figure 2, p. 20. The nuclear magnetic resonance spectrum had absorption at 9.7 p.p.m. (triplet, J~2 c.p.s.), 5.7 p.p.m. (multiplet) and 3.05 p.p.m. (multiplet); integrated 1:2:1, respectively; and integrated for ten total protons relative to two protons at 5.7 p.p.m. (Figure 3, p. 22).

The 2,4-dinitrophenylhydrazone had m.p. 104-5° (literature (35) m.p. 98-9°). A mixed melting point with the 2,4-dinitrophenylhydrazone of Δ^2-cyclopentenylacetaldehyde (from the photolysis of norcamphor) had m.p. 103-5°.

2-(Δ^2-Cyclopentenyl)ethanol (XXXIX) by the lithium aluminum hydride reduction of Δ^2-cyclopentenylacetaldehyde

Δ^2-Cyclopentenylacetaldehyde (250 mg.), from the pyrolysis of bicyclo(3.2.0)hept-6-ene oxide, was reduced with lithium aluminum hydride (50 mg.) in ether (5 ml.). Excess hydride was destroyed with 0.5 ml. of water, and the organo-aluminum complex was hydrolyzed by addition of several drops of 2N hydrochloric acid. The reaction mixture was filtered, and the ether was removed with a rotary film evaporator. The oily residue was distilled, *in vacuo*, in a micro distillation apparatus. An alcohol was obtained (150 mg., infrared (CCl_4): 3670, 3350, 3080, 1615, 1055, 970 and 910 cm^{-1}, Figure 2, p. 20; nuclear magnetic resonance: 5.6 p.p.m. (multiplet), 3.6 p.p.m. (triplet, $J \sim 6.7$ c.p.s.), 2.7 p.p.m. (multiplet); integrates 2:2:1, respectively; integrates for a total of twelve protons relative to two protons at 3.6 p.p.m., Figure 3, p. 22) which was compared to known 2-(Δ^2-cyclopentenyl)-ethanol, prepared by the lithium aluminum hydride reduction of Δ^2-cyclopentenylacetic acid synthesized by the procedure of Noller and Adams (36). The infrared and nuclear magnetic resonance spectra of the two alcohols were superimposable. The α-naphthylurethan of the reduced aldehyde had m.p. 81-3° and showed no mixed melting point depression upon admixture with an authentic sample of the α-naphthylurethan of 2-(Δ^2-cyclopentenyl)ethanol.

2-(Δ^2-Cyclopentenyl)ethanol (XXXIX) by the lithium aluminum hydride reduction of Δ^2-cyclopentenylacetic acid

Δ^2-Cyclopentenylacetic acid (1.0 g., prepared via the procedure of Noller and Adams (36) from 3-chlorocyclopentene and malonic ester) was dissolved in ether and added dropwise to a stirred slurry of lithium aluminum hydride (500 mg.) in ether (50 ml.) and left to stir for several hrs. The excess hydride was quenched with a saturated solution of sodium sulfate in water. Hydrochloric acid (2N) was added to hydrolyze the organo-aluminum complex. The reaction mixture was filtered, and the ether layer was separated and dried over anhydrous sodium sulfate. Evaporation of the ether left a viscous liquid (0.9 g.). Analysis by gas chromatography on a Perkin-Elmer RX column showed one product and some unreacted acid. A sample of the alcohol was collected from the gas chromatograph: Infrared and nuclear magnetic resonance spectra absorption are listed above.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.83; H, 11.09.

The α-naphthylurethan of authentic 2-(Δ^2-cyclopentenyl)-ethanol had m.p. 82-3°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.00; H, 7.00; N, 5.25.

The monoepoxidation of norbornadiene

Following the procedure of Meinwald, Labana and Chadha (37), 7.5 g. (0.04 mole) of 40% peracetic acid (which had previously been treated with 200 mg. of sodium acetate to neutralize any sulfuric acid present) was added to a stirred suspension of 10.6 g. (0.1 mole) of anhydrous sodium carbonate in a solution of 7.4 g. (0.08 mole) of norbornadiene and 65 g. of methylene chloride. The temperature was maintained at 20° during the addition which required 30 minutes. The reaction mixture was allowed to stir for 2 hrs., then filtered, and the filter cake washed with methylene chloride. The solvent was removed under vacuum pressure maintaining the temperature of the residue below 25°. The residue was distilled by the sudden contact of a hot oil bath (120°) with the flask and the immediate application of a strong vacuum pressure to the system. Part of the residue flashed through the distilling apparatus and collected in a collection flask maintained at -70° (Dry Ice-acetone). This material was a semi-solid which became a viscous liquid at room temperature. An infrared spectrum of this material (neat) showed the presence of an epoxide linkage (852 cm^{-1}). The nuclear magnetic resonance spectrum had absorption at 3.5 p.p.m. (triplet, J~1.5 c.p.s.), 3.25 p.p.m. (singlet), 2.9 p.p.m. and 1.3 p.p.m. which integrated 1:1:1:1.

Exo-6-hydroxymethylenebicyclo(3.1.0)hexane (XLV) by the reduction of bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde

A small amount of bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde, obtained from the pyrolysis of bicyclo(3.2.0)hept-6-ene oxide, was collected from the gas chromatograph. This sample was dissolved in ether and added to a stirred slurry of lithium aluminum hydride (50 mg.) in ether (10 ml.) and left to stir for several hours. Water was added to quench excess hydride and hydrolyze the organo-aluminum complex. The ether layer was separated, dried and the ether evaporated leaving 25 mg. of a viscous material. Analysis by gas chromatography on a THEED column at 125° showed that the product was a mixture whose major product had the same retention time as authentic *exo*-6-hydroxymethylenebicyclo(3.1.0)hexane (synthesized by the lithium aluminum hydride reduction of ethyl bicyclo(3.1.0)hexane-*exo*-6-carboxylate) and had no peak corresponding to the *endo* isomer (synthesized by the lithium aluminum hydride reduction of bicyclo(3.1.0)hexane-*endo*-6-carboxylic acid). The major product was collected from the chromatograph for spectral analysis. The infrared spectrum of this compound was identical with that of authentic *exo*-6-hydroxymethylenebicyclo(3.1.0)hexane (see Figure 4, p. 28).

Ethyl bicyclo(3.1.0)hexane-*exo*-6-carboxylate

In a manner similar to that reported by Meinwald, Labana and Chadha, ethyl diazoacetate (5.5 g., 0.048 mole) was added to a suspension of 0.5 g. of copper powder in 18 g. (0.27 mole) of cyclopentene with cooling (37). After addition, the reaction mixture was allowed to warm to room temperature and then refluxed on a steam bath for 24 hrs. Water was added, and the organic layer was separated from the aqueous layer and copper powder. Excess cyclopentene was distilled from the organic layer leaving a viscous residue. Distillation gave a fraction (1.6 g., 21%) boiling at 80-85° (16 mm.). Analysis by gas chromatography on a Perkin-Elmer RX column showed this to be a mixture of three compounds with one predominating over the other two in the relative ratio of 17:3:1. No attempt was made to separate these compounds.

Exo-6-hydroxymethylenebicyclo(3.1.0)hexane (XLV)

Crude ethyl bicyclo(3.1.0)hexane-*exo*-6-carboxylate (0.5 g.) in ether was added dropwise to a slurry of lithium aluminum hydride (0.20 g.) in ether (20 ml.) and left to stir for several hrs. Water was added to quench the excess hydride and hydrolyze the organo-aluminum complex. The ether layer was separated, dried, and the ether evaporated leaving 0.3 g. of a viscous material. Analysis by gas chromatography on a THEED column at 125° showed one major product predominating over two minor products in the ratio of 5:1. The retention time of the major product (4 minutes) was different from that of endo-6-hydroxymethylenebicyclo(3.1.0)hexane (4.8 min.). The lesser of the two minor products had a retention time identical to that of the endo alcohol. A sample of the major alcohol was collected from the chromatograph for spectral analysis (infrared (CCl_4): 3620, 3010, 2930, 2860, 1470, 1448, 1380, 1126, 1067, 1052, 1028, 1015, 993, 888, 871 and 845 cm^{-1}, Figure 4, p. 28; nuclear magnetic resonance: 3.3 p.p.m. (doublet, J~7 c.p.s.), integrates for twelve total protons relative to two protons at 3.3 p.p.m., Figure 5, p. 30).

Endo-6-hydroxymethylenebicyclo(3.1.0)hexane (XLIV)

Bicyclo(3.1.0)hexane-endo-6-carboxylic acid (200 mg.), synthesized by the procedure of Meinwald, Labana and Chadha (37), was added in small portions to a stirred slurry of lithium aluminum hydride (100 mg.) in ether (10 ml.) and left to stir for several hours. Water was added to quench the excess hydride and hydrolyze the organo-aluminum complex. The ether layer was separated, dried, and the ether evaporated yielding 0.2 g. of a viscous material. Analysis by gas chromatography on a THEED column at 125° showed one major product. A sample was collected from the chromatograph for spectral analysis (infrared (CCl_4): 3620, 3010, 2930, 2860, 1480, 1448, 1410, 1380, 1330, 1182, 1039, 1015 (broad), 901 and 866 cm^{-1}, Figure 4, p. 28; nuclear magnetic resonance: 3.5 p.p.m. (doublet, J~7 c.p.s.), integrates for 12 total protons relative to two protons at 3.5 p.p.m., Figure 5, p. 30).

1-Methylcyclohexene (XLVI)

The infrared spectrum of the olefin collected from the pyrolysis of XIII was found to be identical to that of authentic 1-methylcyclohexene, obtained by methyl Grignard addition to cyclohexanone and acid dehydration of the resulting alcohol.

Δ^2-Cyclohexenylacetaldehyde (XLVII)

The lesser of the two major products from the pyrolysis of XIII was Δ^2-cyclohexenylacetaldehyde (infrared (CCl_4): 3030, 2860, 2710, 1725, 1685, 1650, 1435 and 835 cm^{-1}, Figure 6, p. 34; nuclear magnetic resonance: 9.7 p.p.m. (triplet, J~2 c.p.s.), 5.5 p.p.m. (multiplet), integrates 1:2, Figure 7, p. 36).

The 2,4-dinitrophenylhydrazone of XLVII had m.p. 99.5-100.5° (literature (35) m.p. 97°).

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.30. Found: C, 55.18; H, 5.06.

Hydrogenation of XLVII (50 mg.) in ethyl acetate (5 ml.)

with a catalytic amount of 5% palladium on charcoal gave the theoretical uptake of hydrogen in two hours. The 2,4-dinitrophenylhydrazone had m.p. 123.5-5° (reported for the 2,4-dinitrophenylhydrazone of cyclohexylacetaldehyde (39) m.p. 124-5°).

Reduction of Δ^2-cyclohexenylacetaldehyde with lithium aluminum hydride

Δ^2-Cyclohexenylacetaldehyde (100 mg.), obtained from the pyrolysis of XIII, was dissolved in ether (5 ml.) and added to a stirred slurry of lithium aluminum hydride (100 mg.) in ether (10 ml.). After two hours, several drops of water and 2N hydrochloric acid were added to destroy the excess hydride and hydrolyze the organo-aluminum complex. The reaction mixture was filtered and the ether evaporated. A small amount of the resulting alcohol was collected from the gas chromatograph for spectral analysis. The infrared spectrum of this alcohol was compared with that of 2-(Δ^3-cyclohexenyl)ethanol, obtained as a gift from the General Electric Research Laboratories in Schenectady, New York. These spectra are reproduced in Figure 6, p. 34.

3,4-Tetramethylene-2,3-dihydrofuran (L)

The major product from the pyrolysis of XIII was 3,4-tetramethylene-2,3-dihydrofuran (infrared (neat): 2910, 2850, 1670, 1470, 1445, 1100, 1085, 1060, 1040, 940, 920, 835 and

788 cm^{-1}, Figure 8, p. 38; nuclear magnetic resonance: 5.9 p.p.m. (triplet, $J \sim 1.5$ c.p.s.), 4.3 p.p.m. (triplet, $J \sim 9.5$ c.p.s.), 3.7 p.p.m. (triplet, $J \sim 8.7$ c.p.s.), integrates 1:1:1, respectively, Figure 9, p. 40; ultraviolet (95% ethanol): λmax. 214 mμ. ($\epsilon \sim 6100$)).

Hydrogenation of 3,4-tetramethylene-2,3-dihydrofuran

The enol ether (50 mg.) was hydrogenated in ethyl acetate (5 ml.) with a catalytic amount of prereduced 5% platinum oxide on charcoal. In two hours, the theoretical amount of hydrogen was taken up. The mixture was filtered and concentrated under vacuum giving essentially one compound as shown by analysis by gas chromatography on a Perkin-Elmer RX column. The saturated ether collected from the gas chromatograph showed infrared maxima (CCl_4) at 2930, 2860, 2670, 1590, 1480, 1450, 1135, 1082, 1060, 1030, 968, 926, 892 cm^{-1} (Figure 8, p. 38) and nuclear magnetic resonance absorption at 3.6 p.p.m. (multiplet), 2.2 p.p.m. (broad), 1.5 p.p.m. (broad single peak) which integrated 4:2:8 (Figure 9, p. 40).

Cis-3,4-tetramethylenetetrahydrofuran (XLIX, *cis*-hexahydrophthalan)

Following the procedure of Warnell and Shriner for ozonolysis of an olefin (40), bicyclo(4.2.0)oct-7-ene (0.5 g.) in anhydrous ethanol (40 ml.) was cooled in an ice bath and a stream of ozone in oxygen (2%) was passed through the solution for ½ hour. The end-point of the reaction was determined by the sudden liberation of iodine in a potassium iodide trap attached to the system. The ethanol solution was allowed to warm to room temperature and concentrated under vacuum. The crude liquid ozonide was dissolved in ether (5 ml.) and added dropwise to a stirred suspension of lithium aluminum hydride (1.0 g.) in ether (20 ml.). The mixture was allowed to stir for one hour then refluxed for ½ hour. Excess hydride was quenched with water. Hydrochloric acid, 2N (1 ml.), was added and the solution stirred until hydrolysis was complete. The ether solution was filtered and dried over anhydrous sodium sulfate. Removal of the ether under vacuum gave a colorless liquid diol (0.5 g., 70%; infrared (neat): 3350 (broad), 2930, 2860, 1030 (broad) cm^{-1}). A small amount of the diol in ether was induced to crystallize by keeping it in the freezer overnight. The white crystals had m.p. 40-2° (reported for _cis_-hexahydrophthalyl alcohol (67) m.p. 42-3°).

Without further purification, the liquid diol was refluxed with sulfuric acid (2 ml., 18%) for 20 minutes, in a manner similar to that reported (41, 42). The reaction mixture was allowed to cool and then extracted twice with ether. The combined ether layers were dried over anhydrous sodium sulfate. Removal of ether under vacuum left a strong smelling liquid (0.40 g., 91%) which was shown to be essentially one compound by analysis by gas chromatography on a Perkin-Elmer RX column. A small amount of authentic cis-hexahydrophthalan (XLIX) was collected from the gas chromatograph for spectral analysis. Both the infrared and nuclear magnetic resonance spectra of XLIX were identical with those obtained from hydrogenated 3,4-tetramethylene-2,3-dihydrofuran (L). The infrared spectra are reproduced in Figure 8, p. 38.

2,3-Tetramethylenetetrahydrofuran (XLVIII)

Ethyl 2-cyclohexanonylacetate was synthesized via the procedure of Segre, Viterbo and Parisi in 44% yield (68). A solution of 9.1 g. of the keto-ester in ether was added dropwise to a slurry of lithium aluminum hydride (3.0 g.) in ether (250 ml.). The addition took one hour, and the mixture was refluxed for one hour longer. Excess hydride was quenched by addition of a saturated solution of sodium sulfate in water and the organo-aluminum complex was hydrolyzed by the addition of 2N hydrochloric acid. The ether layer was separated and dried over anhydrous sodium sulfate. Evaporation of ether and distillation yielded 5.5 g. (77%) of 2-hydroxyethylenecyclohexanol, b.p. 115° (0.2 mm.), infrared (CCl_4): broad bands at 3300, 1100 and 1050 cm^{-1}).

The diol (1.0 g.) was refluxed with sulfuric acid (3 ml., 18%) for ½ hour. The aqueous mixture was extracted twice with ether, which was then dried over anhydrous sodium sulfate. Evaporation of ether left 0.7 g. of crude product which was shown to be essentially one product by analysis by gas chromatography on a Perkin-Elmer RX column. A sample of the material, collected from the chromatograph for spectral analysis, showed infrared bands at 1145, 1138, 1063, 981, 933 and 858 cm^{-1}.

Norbornene oxide (LVI)

Following the epoxidation procedure of Korach, Nielsen and Rideout (66), norbornene (8.0 g., 0.085 mole), methylene chloride (65 ml.), and anhydrous sodium carbonate (20 g., 0.188 mole) were stirred together in a 250 ml. flask equipped with a thermometer and dropping funnel. To this was added 18 g. of 40% peracetic acid solution (0.095 mole) over ½ hour maintaining the temperature at 20°. The reaction mixture was allowed to stir for two hours, then filtered and the filter cake washed with methylene chloride. The solvent was removed from the filtrate with a rotary film evaporator. The residue was sublimed at atmospheric pressure using an oil bath at 130°. The solid obtained (7.0 g., 75% yield) had m.p. 120-2° (literature m.p. 118-9° (69), 125-7° (70)) and showed an infrared band (CCl_4) at 848 cm^{-1}.

Pyrolysis of norbornene oxide

The solid epoxide (1.0 g., in 50 mg. portions) was dropped onto a column of glass helices in a temperature control oven identical to that reported for the pyrolysis of liquid epoxides and ketones. The column was kept under continuous nitrogen flow except for the momentary periods when the epoxide was added. No pyrolysis was apparent under 500°. The epoxide passed through the column and sublimed in the cold collection tube. Complete conversion was effected at 550°. Products were separated and collected by gas chromatography using a Perkin-Elmer RX column at 125°. The retention times for the major products were: Δ^2-cyclopentenone, 7.0 min.; Δ^3-cyclohexenylcarboxaldehyde, 10.1 min.; and norcamphor, 13.2 min.

Δ^2-Cyclopentenone (LVIII)

The unsaturated ketone from the pyrolysis of LVI had infrared maxima (CCl_4) at 3050, 1716, 1645 and 1610 cm^{-1} (Figure 10, p. 54). The nuclear magnetic resonance spectrum had absorption at 7.6 p.p.m. (multiplet), 6.1 p.p.m. (multiplet), 2.6 p.p.m. (multiplet), 2.2 p.p.m. (multiplet) and integrated 1:1:2:2 (Figure 11, p. 56) and is consistent with that reported for Δ^2-cyclopentenone (48). The ultraviolet spectrum (95% ethanol) had λmax. 215mμ (ϵ>10,000).

The 2,4-dinitrophenylhydrazone of LVIII was deep red and had m.p. 165-6° (literature (49) m.p. 165-6°).

Δ^3-Cyclohexenylcarboxaldehyde (LVII)

A small amount of the major product from the pyrolysis of LVI was collected from the gas chromatograph. The infrared and nuclear magnetic resonance spectra of this product were identical to that of an authentic sample of Δ^3-cyclohexenylcarboxaldehyde (prepared by Diels-Alder addition of acrolein and butadiene) kindly supplied by Dr. H. E. Hennis of the Dow Chemical Company, Midland, Michigan. The infrared spectra had maxima at 3030, 2850, 2710, 1730 and 1645 cm^{-1} (Figure 10, p. 54). The nuclear magnetic resonance spectra had absorption at 9.6 p.p.m. (singlet), 5.4 p.p.m. (multiplet upon expansion) and integrated for ten total protons relative to two protons at 5.4 p.p.m. and one proton at 9.6 p.p.m. (Figure 11, p. 56).

The 2,4-dinitrophenylhydrazone of LVII had m.p. 176-7° (literature (45) m.p. 176-7°). A mixed melting point with an authentic sample gave no depression.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: C, 53.79; H. 4.86. Found: C, 54.12; H, 4.90.

The unsaturated aldehyde (65 mg.) was hydrogenated in ethyl acetate (5 ml.) using a catalytic amount of 5% palladium on charcoal. The theoretical amount of hydrogen for one double bond was absorbed in 4 hours. Filtration and evaporation of the ethyl acetate left a product which gave a 2,4-dinitrophenylhydrazone, m.p. 171-2° (reported for the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde (46) m.p. 172°).

Norcamphor (XXX)

The infrared spectrum of the solid collected from the pyrolysis of norbornene oxide (LVI) was identical to that of known norcamphor (purchased from the Aldrich Chemical Company). The 2,4-dinitrophenylhydrazone had m.p. 131-1.7° (literature (47) m.p. 130-1.5°).

Bicyclo(3.2.0)heptan-exo-6-ol (LXI)

Following the procedure of Brown and Zweifel (52), bicyclo(3.2.0)hept-6-ene (18.2 g., 0.19 mole) in tetrahydrofuran (80 ml.) was placed in a dry three-necked flask equipped with a thermometer, a condenser and a sintered glass dispersion tube. The dispersion tube was connected to the diborane generator. This generator consisted of a two-necked flask equipped with a pressure-equalized dropping funnel (serving alternately as an inlet for nitrogen gas) containing 4.75 g. of sodium borohydride in 125 ml. of diglyme (1.0 M solution). In the generator flask was placed 25 g. (0.18 mole) of boron trifluoride etherate (50% excess) and 16 ml. of diglyme. The air in the apparatus was displaced by nitrogen. Then the diborane, generated by dropwise addition of the sodium borohydride solution to the boron trifluoride etherate, was passed into the olefin-tetrahydrofuran solution (maintained at 0°) by initiating a slight flow of dry nitrogen through the generator. After completion of the sodium borohydride addition (approximately one hour), the generator was heated for one hour on a steam bath, maintaining a slight flow of nitrogen, to ensure the complete transfer of the diborane into the hydroboration flask. After cooling to room temperature, excess hydride was destroyed by the careful addition of water. The organoborane was oxidized by slowly adding 17 ml. of 3N sodium hydroxide, followed by the dropwise addition of 17 ml. of 30% hydrogen peroxide with stirring. The reaction mixture was stirred overnight, then extracted with ether several times. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether yielded 17.0 g. (80%) of bicyclo(3.2.0)heptan-exo-6-ol, infrared (neat): 3330, 2940, 2860, 1072, 1048, 1018, 915 and 840 cm^{-1} (Figure 12, p. 64). The α-naphthylurethan of LXI had m.p. 130-2°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.90; H, 6.97; N, 5.06.

Bicyclo(3.2.0)heptan-6-one (LIX)

Following the procedure of Brown and Garg for oxidation of an alcohol (53), bicyclo(3.2.0)heptan-exo-6-ol (17.0 g., 0.15 mole) and 65 ml. of ether were placed in a 500 ml. flask fitted with a stirrer, condenser and addition funnel. The chromic acid solution, prepared from potassium dichromate (16.0 g., 54 mmole) and 96% sulfuric acid (12.5 ml.) diluted with water to 80 ml., was added to the stirred solution over a period of 15 minutes maintaining the temperature at 25°. The mixture was left to stir for one hour becoming dark blue in color. The ether layer was separated, and the aqueous layer was extracted twice with ether. The combined extracts were washed with saturated sodium bicarbonate, then water. The etherate was dried over anhydrous sodium sulfate. Removal of ether yielded 13.0 g. of crude product. Distillation gave 5.0 g. (30%) of bicyclo(3.2.0)heptan-6-one, b.p. 65-70° (16 mm.), infrared ($CHCl_3$): 1780 cm^{-1}. The semicarbazone derivative had m.p. 200-1.5° (literature (54) m.p. 198.5-201°).

Bicyclo(4.2.0)octan-7-one (LX)

Following the procedure of Brown and Garg for the conversion of olefins to ketones (55), bicyclo(4.2.0)oct-7-ene (3.0 g., 0.028 mole) and lithium borohydride (300 mg.) in ether (25 ml.) were placed in a 100 ml. flask fitted with a stirrer, condenser, addition funnel and thermometer. To the reaction mixture was added 1.0 ml. of boron trifluoride etherate in 4 ml. of ether over a period of 15 minutes at 25°. After two hours, excess hydride was destroyed by the addition of 5 ml. of water. The chromic acid solution, prepared from potassium dichromate (5.0 g., 13.5 mmole) and 96% sulfuric acid (2.5 ml.) diluted with water to 16 ml., was added to the stirred solution over a period of 15 minutes maintaining the temperature at 25°. After heating under reflux for two hours, the upper layer was separated and the aqueous layer extracted twice with ether. The combined ether layer and ether extracts were washed with saturated sodium bicarbonate, then water. Removal of ether and distillation gave 1.2 g. (35%) of bicyclo(4.2.0)octan-7-one, b.p. 55-60° (4 mm.), infrared (neat): 1780 cm^{-1}.

Pyrolysis of bicyclo(3.2.0)heptan-6-one (LIX)

The pyrolysis of bicyclo(3.2.0)heptan-6-one (400 mg.), in a manner previously described, gave a gas and a low boiling liquid. The liquid was analyzed by gas chromatography on a Perkin-Elmer RX column at 75°. The retention time of the liquid was identical to that of cyclopentene. A sample of the liquid was collected from the gas chromatograph. The infrared spectrum was superimposable with that of authentic cyclopentene (purchased from the Aldrich Chemical Company).

Pyrolysis of bicyclo(4.2.0)octan-7-one (LX)

The pyrolysis of bicyclo(4.2.0)octan-7-one (250 mg.), in a manner previously described, gave a gas and a low boiling liquid. The liquid was analyzed by gas chromatography on a Perkin-Elmer RX column at 75°. The retention time of the liquid was identical to that of cyclohexene. A sample of the liquid, collected from the gas chromatograph, had an infrared spectrum which was superimposable with that of authentic cyclohexene (purchased from the Aldrich Chemical Company).

Attempted pyrolysis of norcamphor (XXX)

The solid ketone (0.5 g., in 50 mg. portions, purchased from the Aldrich Chemical Company) was dropped onto a column of glass helices in a temperature control oven in a manner identical to that reported for the pyrolysis of norbornene oxide. At temperatures as high as 550°, the ketone passed through the column and sublimed in the cold collection tube. An infrared spectrum of the collected material was superimposable with that of the starting material.

Experimental for the Photolysis of the Cyclobutanones and Norcamphor

Photolysis of bicyclo(3.2.0)heptan-6-one (LIX)

A 5% solution of bicyclo(3.2.0)heptan-6-one in ether (2.0 g. in 40 ml.) was placed in an internally cooled Pyrex vessel and irradiated with a General Electric UA-3 mercury arc lamp for 24 hours. Analysis by gas chromatography showed that the ketone had decomposed to not less than 10 products. Removal of ether left a gummy, polymeric material. The desired Δ^2-cyclopentenylacetaldehyde was not present as shown by a comparison of retention times on the gas chromatograph using a Perkin-Elmer RX column. The material was not analyzed further.

Photolysis of bicyclo(4.2.0)octan-7-one (LX)

A 10% solution of bicyclo(4.2.0)octan-7-one in ether (1.0 g. in 10 ml.) was placed in an internally cooled Pyrex vessel and irradiated with a General Electric UA-3 mercury arc lamp for 4 hours. Analysis by gas phase chromatography showed that all of the ketone had decomposed. Evaporation of the ether left a polymeric residue. The desired Δ^2-cyclohexenylacetaldehyde was not present as shown by a comparison of retention times on the gas chromatograph using a Perkin-Elmer RX column. The material was not analyzed further.

Photolysis of norcamphor (XXX)

Norcamphor, in concentrations of 5-10%, was irradiated in n-butyl ether, ether and 95% ethanol. The following is a representative procedure.

A 5% solution of norcamphor in 95% ethanol (12 g. in 240 ml.) and a stirring magnet were placed in a water cooled Pyrex immersion well apparatus set on a magnetic stirrer. Irradiation with a quartz jacketed Hanovia immersion lamp gave almost quantitative conversion to one product in 24 hours. Analysis by gas phase chromatography of 30μl. samples at various stages of the irradiation showed that rearrangement was taking place at a steady rate, then slowing slightly past the 50% mark. Little or no side reactions were apparent. Injection of measured aliquot samples into the gas chromatograph on a Perkin-Elmer RX column showed that the final concentration of the photoproduct was almost equal to the initial concentration of starting material. The solvent was removed with a rotary film evaporator. Distillation gave 7.2 g. (60%) of Δ^2-cyclopentenylacetaldehyde (XXXVIII), b.p. 66-9° (31 mm.). Some aldehyde was present in the forerun and 2.5 g. of polymeric material was left in the distilling flask. The product showed infrared absorption (CCl_4) at 3080, 2820, 2720, 1725, 1615, 910 cm^{-1} (Figure 12, p. 64), and nuclear magnetic resonance absorption at 9.7 p.p.m. (triplet, J~2 c.p.s.), 5.7 p.p.m. (multiplet), and 3.1 p.p.m.

(broad multiplet). These peaks integrate 1:2:1 respectively. Integration gives a total of ten protons relative to one proton at 9.7 p.p.m. This spectrum is identical to that of Δ^2-cyclopentenylacetaldehyde from the pyrolysis of XXXVII which is reproduced in Figure 3, p. 22. The semicarbazone of the photoproduct after recrystallization from water had m.p. 115-7° (literature (56) m.p. 116°). The 2,4-dinitrophenylhydrazone of the photoproduct had m.p. 103-5° (literature (35) m.p. 98-9°).

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: C, 53.79; H, 4.86. Found: C, 53.86; H, 4.90.

The aldehyde (XXXVIII) was reduced to the corresponding alcohol (XXXIX) with lithium aluminum hydride in ether. The α-naphthylurethan derivative had m.p. 82-3.5° and showed no mixed melting point depression on admixture with an authentic sample.

Δ^2-Cyclopentenylacetic acid (XL) by the silver oxide oxidation of Δ^2-cyclopentenylacetaldehyde (XXXVIII)

Following the procedure of Campaigne and LeSuer (57), silver oxide was prepared by adding a solution of silver nitrate (7.5 g., 0.045 mole) in water (15 ml.) to a solution of sodium hydroxide (3.5 g., 0.088 mole) in water (15 ml.) with vigorous stirring. The brown semi-solid was cooled in ice. To this mixture was added Δ^2-cyclopentenylacetaldehyde (2.0 g., 0.018 mole) in small portions with stirring.

The reaction mixture was left to stir for 5 minutes after the addition was completed. The black silver suspension was removed by suction filtration and washed with several portions of hot water. The cold combined filtrate and washings were acidified with concentrated hydrochloric acid and extracted several times with ether. The combined extracts were dried over anhydrous sodium sulfate. Removal of ether gave 1.2 g. (52%) of Δ^2-cyclopentenylacetic acid. The infrared spectrum (CCl_4) was superimposable with that of authentic XL, synthesized via the procedure of Noller and Adams (36). The amide derivative, recrystallized from benzene-Skelly D, had m.p. 130-2° (literature (58) m.p. 131.5-2.5°) and showed no mixed melting point depression upon admixture with an authentic sample. The infrared spectrum of the amide (KBr) was consistent with that reported (58) for Δ^2-cyclopentenylacetamide (3360, 3190, 3060, 1660, 1630, 1353, 1320, 1300, 1280, 1235, 1205 and 1155 cm^{-1}).

Experimental for the Rearrangement of Bicyclo(3.2.0)hept-6-ene Oxide with Lithium Aluminum Hydride

Lithium aluminum hydride reduction of bicyclo(3.2.0)hept-6-ene oxide

Bicyclo(3.2.0)hept-6-ene oxide (0.8 g.) in ether (5 ml.) was added dropwise to a stirred slurry of lithium aluminum hydride (500 mg.) in ether (50 ml.). The mixture was allowed to stir for three days. Water was added to destroy the excess hydride and hydrolyze the organo-aluminum complex. The ether layer was filtered and dried over anhydrous sodium sulfate. Evaporation of the ether left 0.8 g. of a viscous material. Analysis by gas phase chromatography on a Perkin-Elmer RX column at 125° showed the product to be a mixture of two compounds in the ratio of 35:65. Samples of both alcohols were collected from the gas chromatograph for spectral investigation. The major alcohol had infrared absorption (neat) at 3330, 1072, 1048, 1018, 915 and 840 cm^{-1} (Figure 12, p. 64). The retention time on a THEED column at 100° was identical to that of bicyclo(3.2.0)heptan-exo-6-ol (LXI), prepared by hydroboration of bicyclo(3.2.0)hept-6-ene. The infrared spectrum of the major alcohol was superimposable with that of LXI.

The minor alcohol had infrared absorption (CCl_4) at 3320, 1377 and 1022 cm^{-1} (Figure 12, p. 64). The nuclear magnetic resonance spectrum ($CDCl_3$) had absorption at 3.6 p.p.m. (multiplet) and 0.9 p.p.m. (doublet, J~6 c.p.s.) which integrated 2:3 and for a total of 14 protons relative to 3 protons at 0.9 p.p.m. (Figure 13, p. 67). The α-naphthylurethan of the minor alcohol had m.p. 91-2° (reported (60) for the α-naphthylurethan derivative of cis-2-methylcyclopentanemethanol (LXII) m.p. 92°, trans isomer m.p. 98°).

Anal. Calcd. for $C_{18}H_{21}O_2N$: C, 76.29; H, 7.47; N, 4.94.

Found: C, 76.15; H, 7.41; N, 4.92.

Reduction of bicyclo(3.2.0)hept-6-ene oxide with deuterated reagents

Four simultaneous experiments were run as described below. Bicyclo(3.2.0)hept-6-ene oxide (1.7 g.) in ether (10 ml.) was added dropwise to each of four flasks. Flasks #1 and #2 contained a stirred slurry of lithium aluminum (0.50 g.) in ether (25 ml.); flasks #3 and #4 contained a stirred slurry of lithium aluminum deuteride (0.50 g., 95%, purchased from Metal Hydrides, Inc.) in ether (25 ml.). The mixtures were left to stir for two weeks. After two weeks with lithium aluminum deuteride there is still 10% of unreacted epoxide whereas the reaction with lithium aluminum hydride goes to completion. Moisture was excluded by the use of calcium chloride drying tubes. Excess hydride was quenched and the organo-aluminum complex hydrolyzed by the addition of deuterium oxide to flasks #2 and #4 and the addition of water to flasks #1 and #3. Each reaction mixture was worked up in an identical manner. The ether layer was separated, filtered and dried over anhydrous sodium sulfate. The ether was evaporated and samples of the primary alcohol collected from the gas chromatograph utilizing a THEED column at 100° for separation. The nuclear magnetic resonance spectra were run in carbon tetrachloride and carefully integrated. The integrated peak areas of the hydroxymethylene, methyl and total proton absorption for the four experiments described above are listed in Table 1, p. 70.

Experimental for the Lewis Acid Rearrangement of the Cyclobutene Oxides

Attempted Lewis acid rearrangements of the cyclobutene oxides

Both bicyclo(3.2.0)hept-6-ene oxide and bicyclo(4.2.0)-oct-7-ene oxide (0.1 g.), in separate experiments, were added to stirred solutions of each of the following: aluminum chloride in ether (100 mg. in 10 ml.), aluminum chloride in acetone (100 mg. in 10 ml.), boron trifluoride etherate in ether (0.1 ml. in 10 ml.), and lithium iodide trihydrate in ether (0.1 g. in 10 ml.). At various intervals, 1.0 ml. aliquots were withdrawn with a pipette and 0.5 ml. of water added with shaking. The ether layer was separated with a syringe and dried over anhydrous sodium sulfate. Samples of the ether layer were injected into the gas chromatograph to determine if rearrangement had taken place. No rearrangement was detected even after refluxing the reaction mixtures for 24 hours.

Lithium iodide rearrangement of bicyclo(4.2.0)oct-7-ene oxide

Bicyclo(4.2.0)oct-7-ene oxide (0.5 g.) was added to a stirred solution of lithium iodide in ether (10 ml., 10%)

prepared by the procedure of Taylor and Grant (63). The reaction mixture was allowed to reflux for 6 hours. After cooling to room temperature, a 1.0 ml. aliquot was withdrawn with a pipette and 0.5 ml. of water added with shaking. The ether layer was separated with a syringe and dried over anhydrous sodium sulfate. A sample was injected into the gas chromatograph using a Perkin-Elmer RX column at 150°. From the retention times of the peaks from the sample, it was obvious that the epoxide was completely destroyed and that two new products had formed. The ether layer from the aliquot was concentrated by passing a stream of nitrogen over it and the residue was injected into the gas chromatograph. Samples of these two products were collected from the gas chromatograph for spectral investigation. The first product had a retention time identical to that of Δ^2-cyclohexenylacetaldehyde (XLVII). The infrared spectrum (CCl_4) was superimposable with that of an authentic sample of XLVII obtained from the pyrolysis of bicyclo(4.2.0)oct-7-ene oxide (Figure 14, p. 77).

The second product had infrared absorption (CCl_4) at 3010, 2860, 2700, 1705, 1665, 1449, 1415, 1290, 1210, 1172, 1117, 1020, 1000 and 858 cm^{-1} (Figure 14, p. 77). The nuclear magnetic resonance spectrum had absorption at 9.1 p.p.m. (doublet, J~4 c.p.s.) and 0.8 p.p.m. (multiplet).

The reaction mixture was chromatographed by towering on a 6 inch column of silica gel and eluting with benzene. Most of the colored material remained on the column while 0.20 g. of a colorless, viscous material was obtained. This material was oxidized by dissolving it in 1.0 ml. of 95% ethanol and adding it to a stirred solution of silver nitrate (1.1 g.) in water (3 ml.) followed by the slow addition of sodium hydroxide (0.4 g.) in water (5 ml.). The reaction mixture was allowed to stir for several hours, then it was carefully acidified with 5N hydrochloric acid and immediately extracted twice with ether. Removal of the ether left a viscous liquid which was dissolved in pentane and put in the freezer overnight. In the morning, white crystals (50 mg.) had formed which had m.p. 79-80°. The reported m.p. for bicyclo(3.1.0)-endo-7-carboxylic acid (LXVIII, endo-7-norcarane carboxylic acid) is 79-80°, whereas the exo isomer is reported to melt at 96° (64). A mixed melting point determination with an authentic sample of LXVIII (kindly supplied by Professor J. A. Berson) had no depression. The infrared spectrum (CCl_4) of the acid was superimposable with that of authentic LXVIII with absorption at 1695, 1305, 1212, 1175, 1108, 975 and 863 cm^{-1} (Figure 14, p. 77).

Gas phase chromatography

Two gas chromatography columns were used extensively, 1. a Perkin-Elmer RX column (a two meter, ¼" diameter column utilizing Ucon oil LB-550-X on diatomaceous earth), and 2. a THEED column (a one meter, ¼" diameter glass column utilizing tetrahydroxyethylene ethylene diamine (THEED) 1:3 on 60/80 Firebrick). The column used, conditions and retention times are listed for the reactions reported:

Pyrolysis of bicyclo(3.2.0)hept-6-ene oxide

bicyclo(3.2.0)hept-6-ene oxide (XXXVII)	column 1	125°, 15 p.s.i.	8.5 min.
unidentified enol ether			5.2
Δ^2-cyclopentenylacetaldehyde (XXXVIII)			7.4
bicyclo(3.1.0)hexane-*exo*-6-carboxaldehyde (LIII)			12.0
2-(Δ^2-cyclopentenyl)-ethanol (XXXIX)	1	175°, 20 p.s.i.	7.0
Δ^2-cyclopentenylacetic acid (XL)			17.0
ethyl bicyclo(3.1.0)hexane-*exo*-6-carboxylate			7.0
exo-6-hydroxymethylenebicyclo(3.1.0)hexane (XLV)	(a) 2 (b) 2	150°, 15 p.s.i. 125°, 15 p.s.i.	2.0 4.0
endo-6-hydroxymethylenebicyclo(3.1.0)hexane (XLIV)	(a) (b)		2.5 4.8

Pyrolysis of bicyclo(4.2.0)oct-7-ene oxide

bicyclo(4.2.0)oct-7-ene oxide (XIII)	1	150°, 15 p.s.i.	10.4
1-methylcyclohexene (XLVI)			1.6
3,4-tetramethylene-2,3-dihydrofuran (L)			7.0

Δ^2-cyclohexenylacetaldehyde (XLVII)			9.1
bicyclo(4.1.0)heptan-1-carboxaldehyde (LI)			12.0
cis-hexahydrophthalan (XLIX)	1	175°, 15 p.s.i.	5.4
Pyrolysis of norbornene oxide (LVI)			
Δ^2-cyclopentenone (LII)	1	125°, 15 p.s.i.	7.0
Δ^3-cyclohexenylcarboxaldehyde (LVII)			10.1
norcamphor (XXX)			13.2
Pyrolysis of bicyclo(3.2.0)heptan-6-one and bicyclo(4.2.0)octan-7-one			
bicyclo(3.2.0)heptan-6-one (LIX)	1	150°, 15 p.s.i.	8.2
bicyclo(4.2.0)octan-7-one (LX)			10.2
cyclopentene	1	75°, 10 p.s.i.	4.2
cyclohexene			4.7
Photolysis of norcamphor			
norcamphor (XXX)	1	150°, 15 p.s.i.	7.0
Δ^2-cyclopentenylacetaldehyde (XXXVIII)			4.2
Lithium aluminum hydride reduction of bicyclo(3.2.0)hept-6-ene oxide			
cis-2-methylcyclopentane-methanol (LXII)	2	100°, 10 p.s.i.	4.6
bicyclo(3.2.0)heptan-*exo*-6-ol (LXI)			8.7
Lithium iodide rearrangement of bicyclo(4.2.0)oct-7-ene oxide			
bicyclo(4.2.0)oct-7-ene oxide	1	150°, 15 p.s.i.	9.4
Δ^2-cyclohexenylacetaldehyde (XLVII)			8.7
bicyclo(4.1.0)heptan-*endo*-7-carboxaldehyde (LIV)			14.8

SUMMARY

It has been known for many years that heat or Lewis acids can cause epoxides to rearrange. The pyrolysis (420^{o}) of bicyclo(3.2.0)hept-6-ene oxide (I), synthesized by the peracid oxidation of bicyclo(3.2.0)hept-6-ene, gives a 50% yield of Δ^{2}-cyclopentenylacetaldehyde (II) and a small amount of bicyclo(3.1.0)hexane-exo-6-carboxaldehyde (III). The pyrolysis (400^{o}) of bicyclo(4.2.0)oct-7-ene oxide (IV) gives 3,4-tetramethylene-2,3-dihydrofuran (V), Δ^{2}-cyclohexenylacetaldehyde (VI) and 1-methylcyclohexene (VII) in the ratio of 56:31:13, respectively. The pyrolysis of norbornene oxide (550^{o}) gives Δ^{3}-cyclohexenylcarboxaldehyde (VIII), norcamphor (IX) and Δ^{2}-cyclopentenone (X) in yields of approximately 65, 8, and 8%, respectively.

The pyrolysis of bicyclo(3.2.0)heptan-6-one (420^{o}) and bicyclo(4.2.0)octan-7-one (400^{o}) give cyclopentene (XI) and cyclohexene (XII), respectively. Norcamphor is unaffected at temperatures as high as 550^{o}. The photolysis of norcamphor gives II in good yield. The structures of all of the above compounds were rigorously proven by both chemical and spectroscopic means. Δ^{2}-Cyclopentenylacetic acid and 2-(Δ^{2}-cyclopentenyl)ethanol were synthesized and compared to the corresponding acid and alcohol obtained from II. Exo and endo-6-hydroxymethylenebicyclo(3.1.0)hexane were synthesized and compared with the alcohol obtained by the reduction of III.

Cis-hexahydrophthalan was synthesized and found to be identical to dihydro V. Authentic samples were used for the comparison of VII, VIII, IX, X and XI.

The reduction of I with lithium aluminum hydride in ether gives two alcohols in the ratio of 65:35. The major alcohol is bicyclo(3.2.0)heptan-exo-6-ol (XIII), as shown by synthesis via hydroboration of bicyclo(3.2.0)hept-6-ene. The unexpected minor alcohol is cis-2-methylcyclopentanemethanol (XIV). Reduction of I with lithium aluminum deuteride and work up with both deuterium oxide and water shows that the formation of XIV proceeds via cleavage of the C-C bond of the epoxide (I) with the formation of a carbon-aluminum bond. This study was based on the integration of peak areas in the nuclear magnetic resonance spectra of the deuterated alcohols.

Lithium iodide in ether reacts with IV to give VI and bicyclo(4.1.0)heptan-endo-7-carboxaldehyde (XV). The structure of XV was proven by oxidation to the corresponding known acid. This suggests that the Lewis acid-catalyzed rearrangement of epoxides proceeds stereospecifically with inversion at the migration terminus.

Possible mechanisms for all of the above rearrangements are discussed. Gas phase chromatography was used extensively in all of the above reactions for the separation, collection and identification of compounds.

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