

1963

I Rearrangement in borate pyrolysis II Photochemical transformations of cycloheptadienes and cycloheptatrienes

George Wayne Borden
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I. REARRANGEMENT IN BORATE PYROLYSIS.
II. PHOTOCHEMICAL TRANSFORMATIONS OF
CYCLOHEPTADIENES AND CYCLOHEPTATRIENES.

Iowa State University of Science and Technology
Ph.D., 1963
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I. REARRANGEMENT IN BORATE PYROLYSIS
II. PHOTOCHEMICAL TRANSFORMATIONS
OF CYCLOHEPTADIENES AND CYCLOHEPTATRIENES

by

George Wayne Borden

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

Major Subject: Organic Chemistry

Approved:

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In Charge of Major Work

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1963

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I. REARRANGEMENT IN BORATE PYROLYSIS

INTRODUCTION

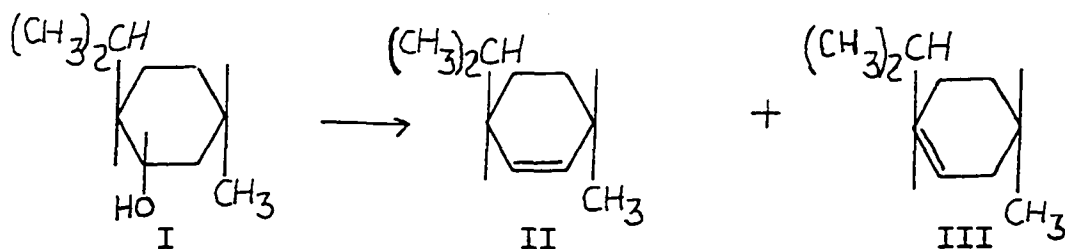
This investigation constitutes a study of the mechanism of borate pyrolysis. An interest in the utilization of borate pyrolysis led to an investigation of the structural integrity of the reaction in systems prone to carbonium ion rearrangements. The findings are not consistent with the previously proposed cis- elimination mechanism and are interpreted on the basis of ionization of the borate esters.

HISTORICAL

In 1950 Brandenburg and Galat (1) reported a new method for the preparation of olefins from alcohols in excellent yield (85-95%) by the use of boric acid. This method was applicable to primary, secondary and tertiary alcohols. The procedure consisted of heating equal molar quantities of boric acid and alcohol to 350°. The authors concluded that this method was similar to the pyrolysis of acetates and that the mechanism involved two steps: (a) formation of the borate ester; (b) decomposition of the ester to olefin and boric acid.

The alcohols studied were n-hexanol, 2-ethylhexanol, n-heptanol, n-octanol, 2-octanol, cyclohexanol, and 1-phenylethanol. Whether the olefins obtained had a double bond in the 1,2- or 2,3 position or were a mixture of isomers was not determined.

O'Connor and Nace (2) reported in 1955 that when equal molar quantities of 1-menthol (I) and boric acid were heated to 150-180°, two moles of water were formed and upon raising the temperature to 270° a mixture of olefins distilled (yield 92-83%). The mixture consisted of Δ^2 -menthene (II) (9-13%) and Δ^3 -menthene (III) (93-87%). The Δ^3 -menthene formed in the reaction was approximately 70% racemized.



When a sample of Δ^3 -menthene, prepared from 1-menthyl S-methylxanthate by the Chugaev reaction, is heated at 270° with metaboric acid the Δ^3 -menthene is partially racemized (10%). A sample of Δ^2 -menthene, prepared from 1-menthyl chloride and sodium methoxide, is not racemized when treated in a similar manner (2).

The authors (2) concluded that the predominance of Δ^3 -menthene suggests that the metaborate ester (monomer or trimer) decomposes by a cis-elimination* and the Δ^3 -menthene was racemized by metaboric acid following its formation. The formation of Δ^2 -menthene can arise by either a cis- or trans-elimination.

In 1956 Dev (4) applied this reaction to the dehydration of cyclopentanol, cyclohexanol, and cycloheptanol. The order

*A referee proposed that the Δ^3 -menthene might be formed by an ionic or solvolytic mechanism rather than a cis-elimination. This would be analogous to a recent report of Cram and Sahyun (3) concerning the generation of 2-phenyl-2-butyl cations in glacial acetic acid. They suggest that the leaving group remains associated with the carbonium ion formed long enough to effect the behavior of the ion, and the leaving group in some cases abstracts a proton from the carbonium ion.

of decomposition temperatures is cyclohexanol > cycloheptanol > cyclopentanol. The relatively low temperatures required, the excellent yields obtained, and the ease of formation of the metaborate prompted the statement that: "The pyrolysis of borate esters should prove to be the method of choice for the dehydration of alcohols, especially secondary and primary."

(4)

During the course of the author's investigation of the mechanism of the borate pyrolysis an instance of rearrangement in borate pyrolysis was reported by Baumgartner and Wilson (5). Pyrolysis of the borate of tetrahydrofurfuryl alcohol (IV) gives dihydropyran (V). In contrast, pyrolysis of the acetate gives the normal olefin (VI).

DISCUSSION

Borate pyrolysis has been shown to be a useful method for the preparation of olefins (1,2,4). Mechanistically, the reaction has been considered a cis-elimination (2,4) analogous to the acetate and xanthate pyrolysis. From an experimental point of view the reaction is simple to carry out, proceeds at relatively low temperatures compared with acetate pyrolysis, and gives excellent yields of olefins. An interest in the mechanism of the borate pyrolysis led to an investigation of systems prone to carbonium ion rearrangements.

The method employed in this study is that used by O'Connor and Nace (2). Equal molar quantities of alcohols and boric acid were warmed slowly to 120-140^o; the water which distilled was separated. The borates formed on further heating decomposed at 250-290^o. The olefins which distilled were collected in a Dry Ice-acetone trap. The crude olefinic product was analyzed by vapor phase chromatography. The peak area was read from the simultaneous trace of a mechanical integrator. Each product was separated by preparative scale vapor phase chromatography and identified by comparison of infrared absorption and vapor phase chromatographic retention time with an authentic sample.

In order to compare pyrolysis of borate esters with an acid catalyzed elimination reaction some alcohols were decomposed in the presence of oxalic acid following the procedure

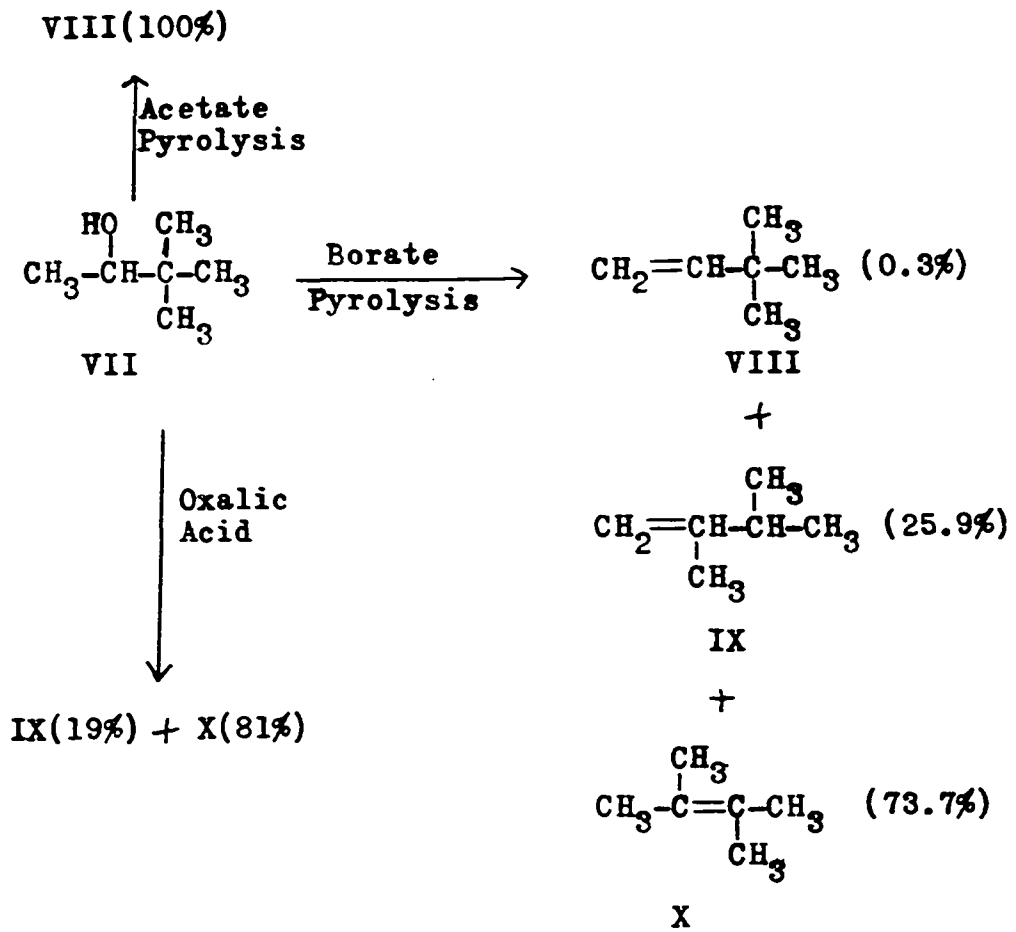
of Whitmore and Rothrock (6). The alcohols studied were 3,3-dimethyl-2-butanol, borneol, cyclohexylcarbinol, and cyclobutylcarbinol. The findings are not consistent with the previously proposed cis-elimination mechanism (2).

Pyrolysis of the borate of 3,3-dimethyl-2-butanol (VII) gives three olefins, (92-96% yield); 3,3-dimethyl-1-butene (VIII, 0.3%), 2,3-dimethyl-1-butene (IX, 25.9%), and 2,3-dimethyl-2-butene (X, 73.7%). Authentic 3,3-dimethyl-1-butene (VIII) was prepared by pyrolysis of 3,3-dimethyl-2-butyl acetate (6). The product from the acetate pyrolysis was shown to be homogeneous by vapor phase chromatography. 2,3-Dimethyl-1-butene (IX) and 2,3-dimethyl-2-butene (X) were obtained by oxalic acid dehydration of (VII) (6). The products were separated by vapor phase chromatography and identified by their nuclear magnetic resonance spectra. The nuclear magnetic resonance spectrum of 2,3-dimethyl-1-butene (IX, 19%) shows a six-proton doublet ($J=6.5$ c.p.s.) at 8.9τ (isopropyl methyls), a one proton multiplet at 7.77τ (isopropyl C-H), a three-proton resonance at 8.32τ ($\text{CH}_3 - \text{C} = \text{C} -$) and a two-proton resonance at 5.23τ ($\text{C}=\text{CH}_2$). Nuclear magnetic resonance spectra of 2,3-dimethyl-2-butene (X) shows only an intense singlet at 8.38τ .

Pyrolysis of the borate of cyclobutylcarbinol (XI) gives cyclopentene (XII).

Borneol (XIII) on pyrolysis of the borate gives camphene (XIV) in 81% yield. This yield is corrected for the borneol

Figure 1. Equations illustrating the reactions of
3,3-dimethyl-2-butanol (VII)

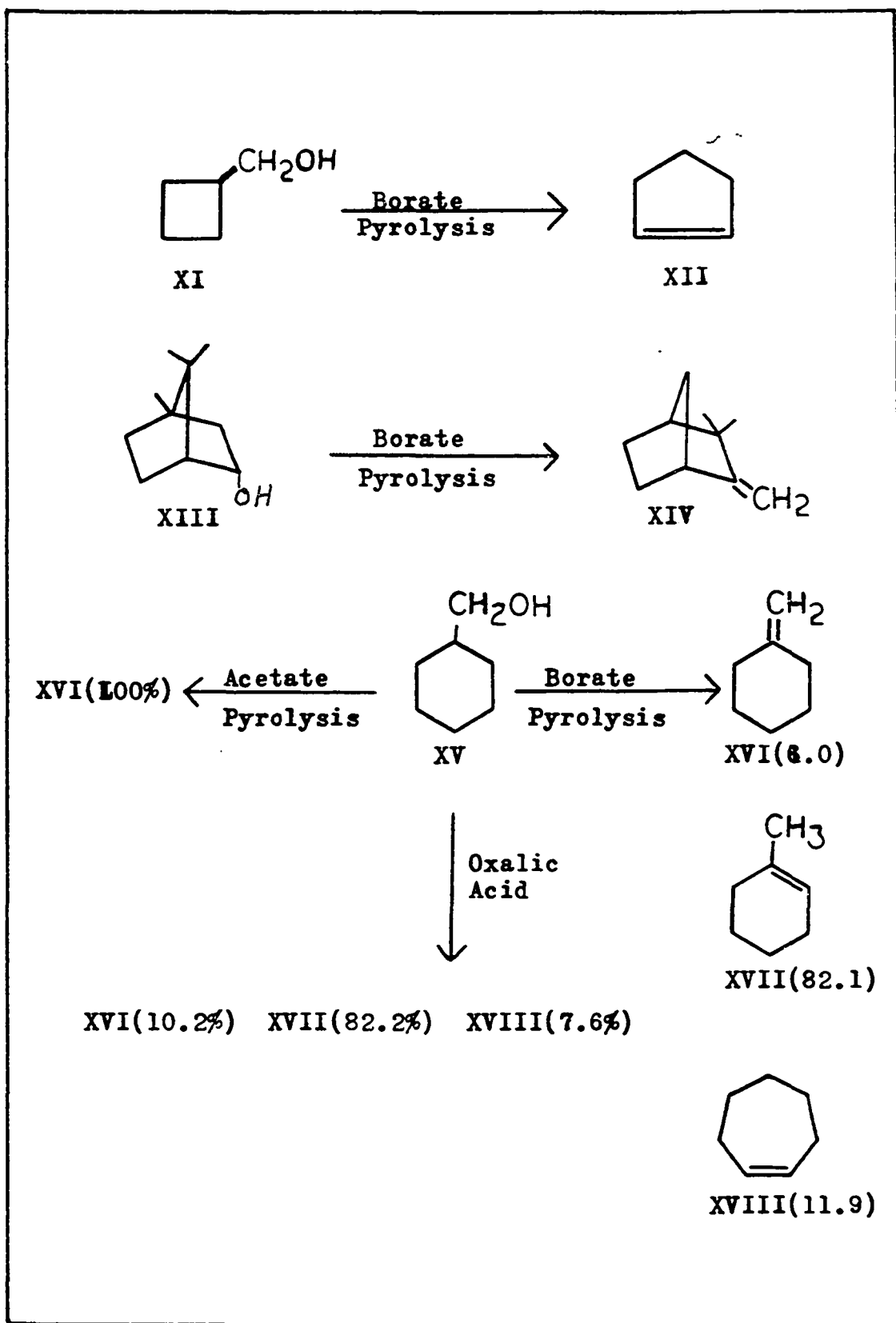


that sublimed from the reaction vessel during borate formation.

Pyrolysis of the borate of cyclohexylcarbinol (XV) gives methylenecyclohexane (XVI, 6%), 1-methylcyclohexene (XVII, 82.1%), and cycloheptene (XVIII, 11.9%).* Cyclohexylcarbinol was dehydrated with oxalic acid to obtain an indication of the product ratios in a simple carbonium ion process. This dehydration gives XVI (10.2%), XVII (82.2%), and XVIII (7.6%). Pyrolysis of cyclohexylcarbiny acetate gives exclusively methylenecyclohexane (XVI) (7,8). The products obtained in the pyrolysis of the borates of 3,3-dimethyl-2-butanol (VII), cyclobutylcarbinol (XI), borneol (XIII), cyclohexylcarbinol (XV) and the results obtained by Baumgartner and Wilson (5) for tetrahydrofurfuryl alcohol raise an interesting question concerning the mechanism of this reaction. The results of these borate pyrolyses leave no doubt that the principal products are formed in a carbonium ion type rearrangement. Rearrangement might proceed by any of three processes: (a) isomerization of the alcohol before or during borate formation, (b) isomerization of an olefin produced by a cis-elimination, or (c) ionization of the borate ester. Isomerization before or during borate formation has been excluded as a possibility in the case of 3,3-dimethyl-2-butanol (VII) and cyclohexylcarbinol (XV). The borates from each of these

*Samples of methylenecyclohexane and 1-methylcyclohexene were furnished by Professor C. H. DePuy.

Figure 2. Equations illustrating the reactions of cyclobutylcarbinol (XI), borneol (XIII), and cyclohexylcarbinol (XV).

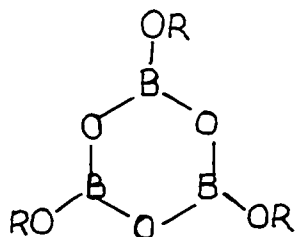


alcohols were heated to 20° below their pyrolysis temperature, cooled, and dissolved in methanol giving unchanged starting alcohol. Ring expanded products such as XII and XVIII would not be expected to predominate in the acid catalyzed isomerization of the exocyclic olefins produced from a cis-elimination of the borates of XI and XV. It might be argued, however, that ring expanded olefins are formed by a direct ionization mechanism while other products are formed by the isomerization of the exocyclic olefins. This cannot be the case, for pyrolysis of the borates of cyclobutylcarbinol (XI) and tetrahydrofurfuryl alcohol give exclusively ring expanded products. In the case of VII and XV the product ratios in the borate pyrolysis are very comparable to the product ratios in the acid-catalyzed dehydration of VII and XV, strongly suggesting a common course for these reactions. These results suggest that the products formed in borate pyrolysis are the result of ionization of the borate ester. The borate melt should be a sufficiently polar medium to permit ionization at elevated temperatures.* The ionization of the borate may involve ion pairs or more completely separated ions. In any event the olefins are derived from a carbonium ion sufficiently free to rearrange.

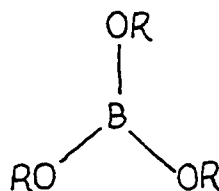
The species which ionizes is of some interest. This is

*This point has been considered previously (see footnote 10, ref. 2).

most likely the metaborate or the metaborate trimer. Metaborates decompose thermally at about 270° (2). Orthoborates, in contrast, are thermally stable well above 330° (5). O'Connor and Nace have shown that heating equimolar quantities of cyclohexanol and boric acid gives the trimer of cyclohexyl metaborate, and that at 218° (melting point of anthracene) no more than 6% monomeric cyclohexyl metaborate is present (2). It seems unlikely, at first, that a metaborate trimer (XIX) would ionize more readily than an orthoborate (XX).

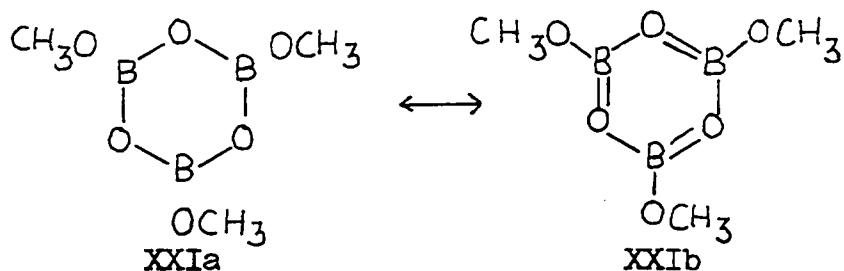


XIX



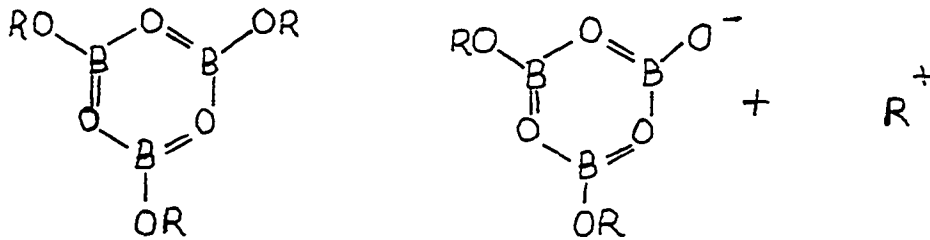
XX

The planar structure of the B_3O_3 ring in trimethyl boroxole as determined by electron diffraction (9) suggests that the resonance from (XXIb) is significant in the description of methyl metaborate trimer.



The ionization of a metaborate trimer to the anion and a carbonium ion then appears in a more favorable light. The anion of the borate trimer is isoelectronic with phenoxide

ion, and indeed similar resonance structures may be written for the metaborate trimer anion.



The stabilization of the metaborate trimer anion is not great but easily accounts for the more facile ionization of metaborate trimers relative to orthoborates.

The results described in the preceding pages show rearranged products predominate (94-100%) in each case. This fact severely limits the potential application of borate pyrolysis in synthesis.

Figure 3. Nuclear magnetic resonance spectrum of 2,3-dimethyl-1-butene (IX)

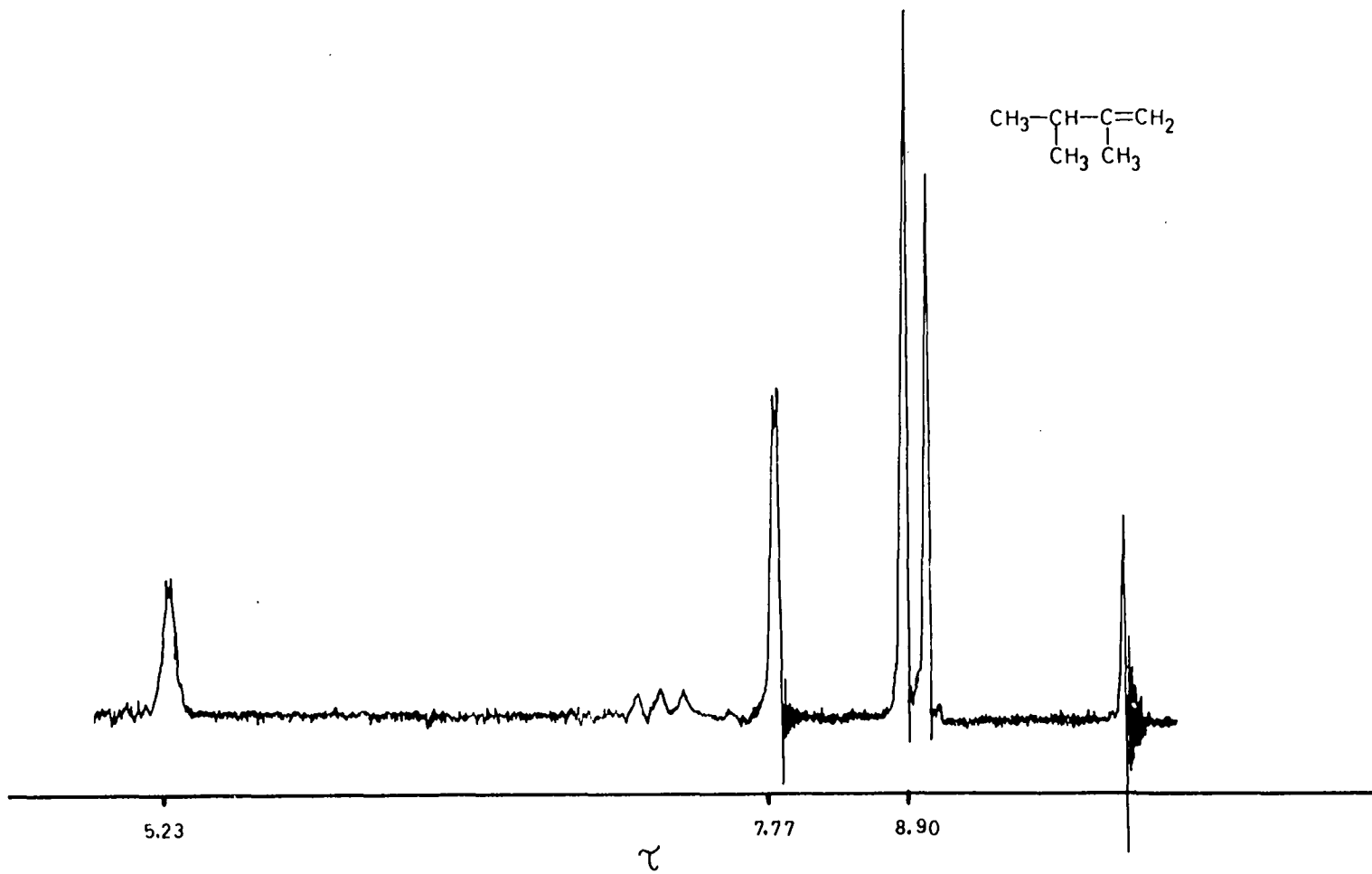
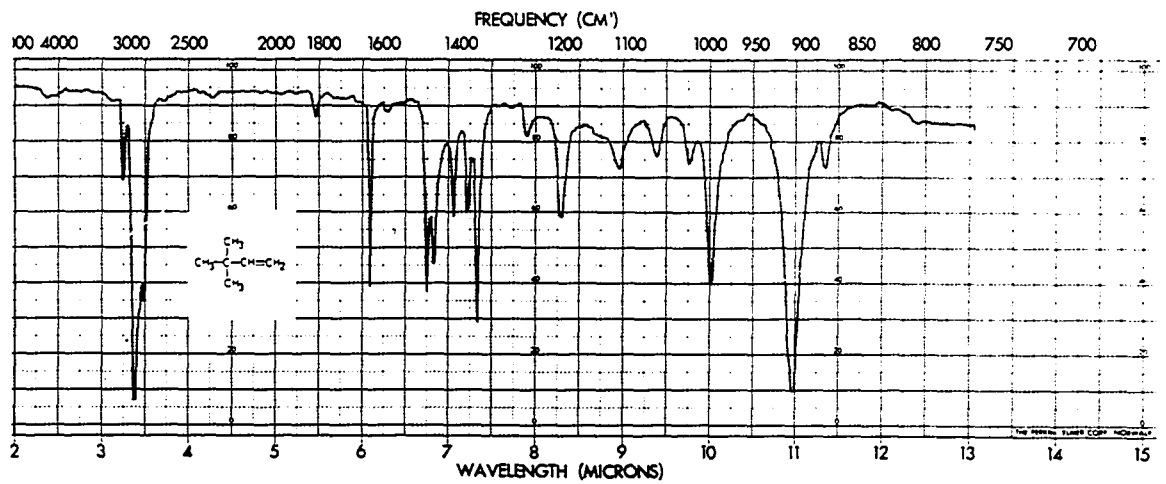
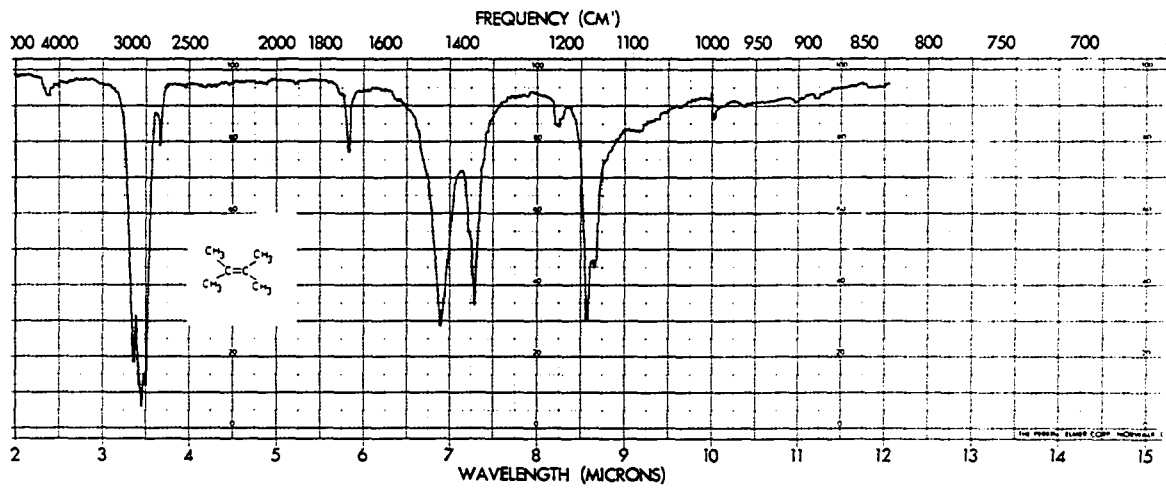
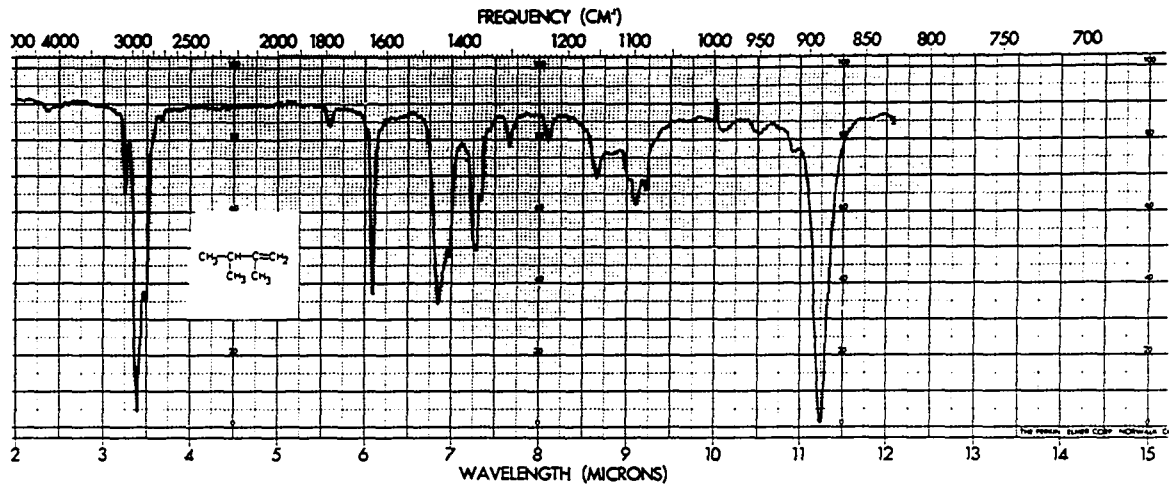


Figure 4. Infrared spectra

top: 2,3-Dimethyl-1-butene

middle: 2,3-Dimethyl-2-butene

bottom: 3,3-Dimethyl-1-butene



EXPERIMENTAL

Experimental for Rearrangement in Borate Pyrolysis

Pyrolysis of 3,3-Dimethyl-2-butyl Borate A mixture of 3,3-dimethyl-2-butyl alcohol (10.0 g., 0.098 mole) and boric acid (6.06 g., 1.098 mole) was slowly heated to 120°. The water which distilled during this time was collected. The mixture was refluxed gently for one hour, and the temperature of the heating bath was slowly raised to 260°. At this temperature the olefins began to distill. After one hour the reaction was complete; the yield was 7.6-7.9 g. of crude olefin (92-96%). The crude olefin product was analyzed by vapor phase chromatography on a 2 meter Perkin-Elmer R column at 52°.

| Run/Product | VIII | IX | X |
|-------------|------|------|------|
| 1 | 0.4 | 25.1 | 74.5 |
| 2 | 0.5 | 24.9 | 74.6 |
| 3 | 0.1 | 27.8 | 72.1 |
| Average | 0.3 | 25.9 | 73.7 |

Pyrolysis of 3,3-Dimethyl-2-butyl Acetate (6) Pure 3,3-dimethyl-2-butyl acetate was dropped slowly through a vycor tube packed with glass helices maintained at 500°. The product was collected in a Dry-Ice acetone cooled trap. The product was separated from acetic acid by trap to trap distillation in a vacuum line. The yield of 3,3-dimethyl-1-butene (homogeneous in vapor phase chromatography) was 4.5 g. (90%).

Oxalic Acid-Catalyzed Dehydration of 3,3-Dimethyl-2-butanol (VII) A mixture of 3,3-dimethyl-2-butanol (8 g.) and oxalic acid (30 g.) was slowly heated to 100-110°. A mixture of water and olefins distilled. The yield of crude olefin (after drying over anhydrous magnesium sulfate) was 6.3 g. (94%). The crude olefin was analyzed by vapor phase chromatography. The products were identified by comparison of infrared spectra with authentic samples.

| Run/Product | IX | X |
|-------------|------|------|
| 1 | 16 | 84 |
| 2 | 21 | 79 |
| 3 | 21.8 | 78.2 |
| Average | 19.6 | 80.4 |

Pyrolysis of Bornyl Borate A mixture of borneol (20 g., 0.13 mole) and boric acid (8 g., 0.13 mole) was heated until water no longer distilled. During this period some borneol (4 g.) sublimed up the distilling head, and it was necessary to change distillation heads before pyrolysis of the borate. When the bath temperature reached 260°, olefin began to distill. The crude product (11 g.) was dried over anhydrous sodium sulfate. The infrared spectrum of the product was identical to that of authentic camphene. Vapor phase chromatography showed the camphene to be at least 96% pure.

Pyrolysis of Cyclohexylcarbinol Borate A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was heated

slowly to 140° and the water which distilled was separated. The bath temperature was then raised to 290°. At this temperature the olefinic product began to distill. The yield of olefinic product began to distill. The yield of olefinic product was 3.8 g. (91%). Analysis of the olefin mixture by vapor phase chromatography on a two meter Perkin-Elmer R Column at 100° gave the results shown below. The two analyses are based on separate experiments and are not duplicate analyses of the same mixture. The olefins were separated by preparative scale vapor phase chromatography and identified by comparison of infrared spectra with authentic samples.

| Run/Product | XVI | XVII | XVIII |
|-------------|-----|------|-------|
| 1 | 5.9 | 82.3 | 11.8 |
| 2 | 6.1 | 81.9 | 12.0 |
| Average | 6.0 | 82.1 | 11.9 |

Oxalic Acid Dehydration of Cyclohexylcarbinol (XV)

A mixture of cyclohexylcarbinol (5 g.) and oxalic acid (30 g.) was slowly heated to 135°. At this temperature water and olefinic product distilled. The yield of olefinic product (after drying) was 3.9 g. (92%). This mixture (analyzed as above) contained methylenecyclohexane (10.2%), 1-methylcyclohexene (82.2%) and cycloheptene (7.6%).

Pyrolysis of Cyclobutylcarbinyl Borate

A mixture of cyclobutylcarbinol (0.8 g.) and boric acid (0.58 g.) was slowly heated to 140° and maintained at this temperature until water no longer distilled. The bath temperature was then slowly

raised to 245-255°. At this temperature the olefinic product distilled smoothly. The product was shown to be a single olefin by vapor phase chromatography (Perkin-Elmer R column, 34°). The infrared spectrum of the product was identical to that of authentic cyclopentene.

Formation and Hydrolysis of Cyclohexylcarbinyl Borate

A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was slowly heated to 140°, and the water which distilled was separated. The bath temperature was then raised to 290° and maintained at this temperature for ten minutes. The mixture was cooled and 100 ml. of methanol and 3 ml. of water were added. This solution was refluxed on the steam bath for 3 hours, and the methanol was removed. The residue was dissolved in ether and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged cyclohexylcarbinol identical in infrared absorption with an authentic sample.

Formation and Hydrolysis of 3,3-Dimethyl-2-butyl Borate

A mixture of 3,3-dimethyl-2-butanol (10 g.) and boric acid (6 g.) was heated slowly to 120° and the water which distilled was separated. The bath temperature was then raised to 250° and maintained for 10 minutes at this temperature. After cooling, the borate was dissolved in 100 ml. of methanol and 3 ml. of water. This solution was refluxed for one hour, and the methanol was removed. The residue was taken up in ether

and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged 3,3-dimethyl-2-butanol identical in infrared absorption to the starting alcohol.

II. PHOTOCHEMICAL TRANSFORMATIONS OF
CYCLOHEPTADIENES AND CYCLOHEPTATRIENES

INTRODUCTION

Photochemical reactions have been known and studied for many years but during the past five years a rapidly growing body of knowledge concerning the mechanism of photochemical reactions has come into existence. This investigation concerns the photochemical reactions of some simple cyclic dienes and trienes. These reactions are new and unique and mechanisms are proposed to explain these anomalies.

HISTORICAL

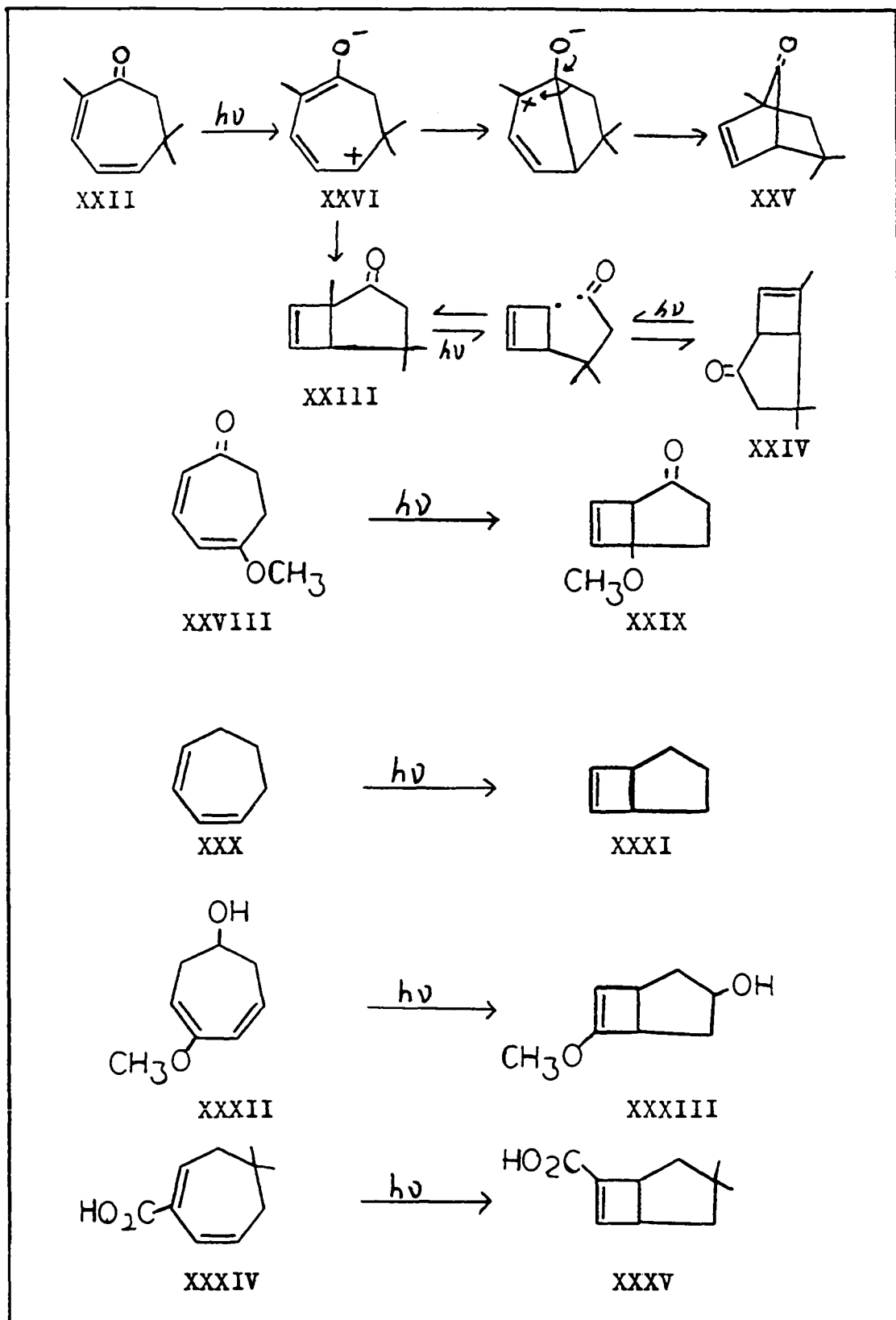
Irradiation of eucarvone (XXII) under various conditions produces three photoisomers (10, 11). Irradiation of eucarvone (XXII) in neutral solutions using a mercury arc lamp gives photoisomers XXIII and XXIV (10). Exposure of eucarvone in aqueous acetic acid to sunlight gives approximately equal amounts of XXIII, and a new bicyclic product, XXV (11).

Irradiation of either XXIII or XXIV establishes a photo-stationary state between these bicyclic ketones (10). The formation of XXIII and XXV may be interpreted as arising from the dipolar excited state XXVI. Photoproducts XXIII and XXIV may be produced from photochemical cleavage (XXVII) of the bond attached to the saturated carbonyl group. Similarly, irradiation of 5-methoxy-2,4-cycloheptadienone (XXVIII) gives the bicyclic ketone (XXIX) (12).

Irradiation of 1,3-cycloheptadiene (XXX) gives the bicyclic photoisomer XXXI in 58% yield (12, 13). 4-methoxy-3,5-cycloheptadienol (XXXII) (12) and dihydrothujic acid (XXIV) (14) each give the corresponding bicyclic photoproducts XXXIII and XXXV. Substituents on the diene seem to exert little effect on the photoisomerization of 1,3-cycloheptadienes. Photocyclization of cycloheptadienes constitutes an important synthetic entry to the [3.2.0]-bicycloheptene series.

In 1951 Grewe and Wulf reported (15) that exposure to sunlight of an aqueous solution of colchicine (XXXVI) gives

Figure 5. Structures and reactions discussed in
the historical section



three photoproducts: alpha- (XXXVII), beta- (XXXVIII), and gamma-lumicolchicine (XXXIX). This constituted the first example of a photoisomerization of a tropolone system.

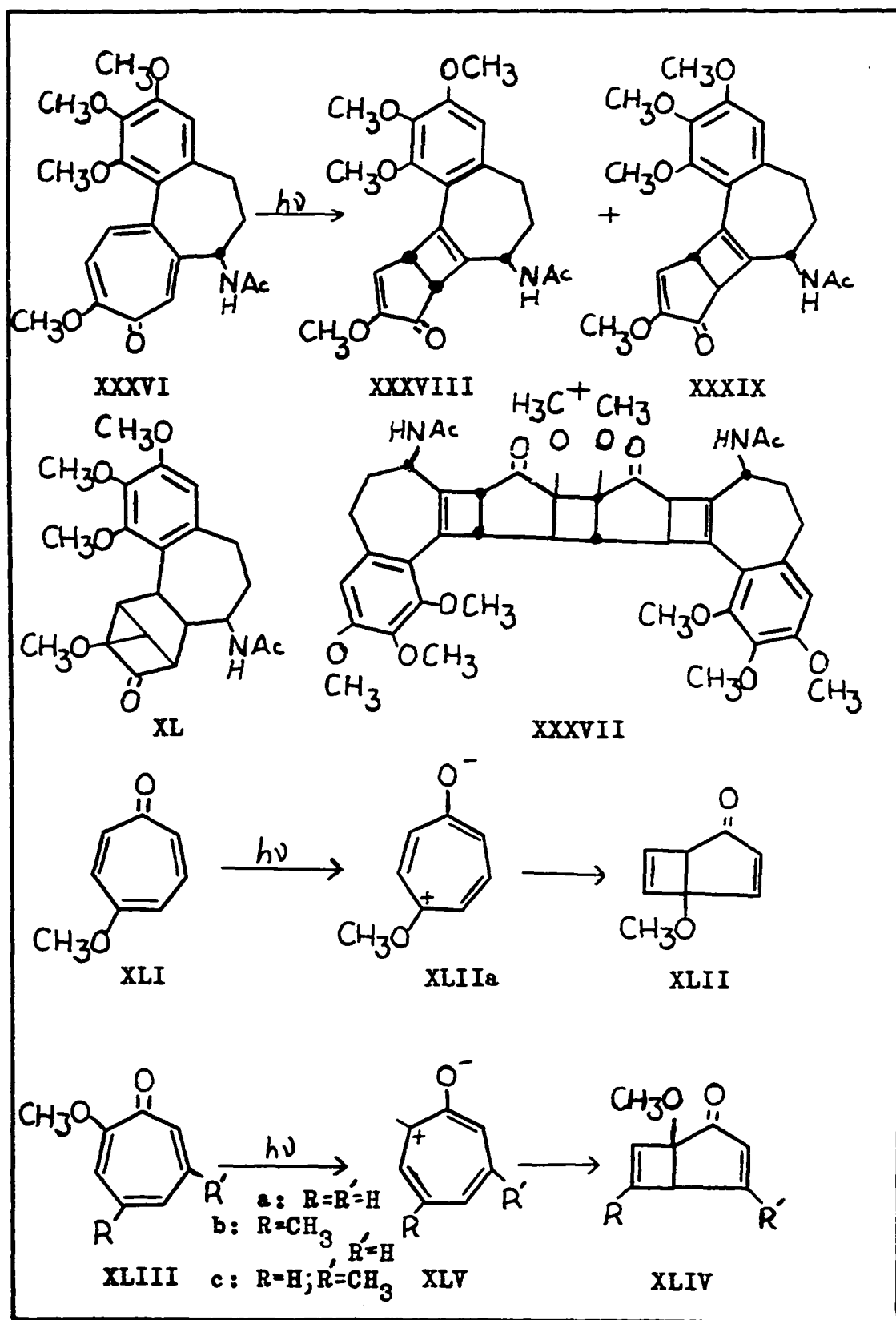
Forbes (16) and Gardner *et al.* (17) established the structure of beta- and gamma-lumicolchicine as XXXVIII (16) and XXIX (17). Schenk proposed in 1961 structure XL for alpha-lumicolchicine (18); later the same year Chapman and Smith showed in fact that the structure of alpha-lumicolchicine was XXXVII, a photodimer of beta-lumicolchicine (XXXVIII) (19).

In 1960 Chapman and Pasto (20) reported the first example of the photoisomerization of a simple troponoid system. Irradiation of γ -tropolone (XLI) methyl ether gives the bicyclic photoisomer XLII (20). Similarly, irradiation of α -tropolone methyl ethers (XLIIIa,b,c) gives the bicyclic photoproducts XLIVa,b,c (21). These isomerizations have been interpreted in terms of the dipolar intermediates XLIIa and XLVa,b,c.

Irradiation of α -tropolone (XLVIa) or its methyl ether (XLVIb) in aqueous solution gives XLVIIa,b (22). The mechanistic path of this reaction has been established by investigation of XLVIb and 4- and 6-methyltropolone methyl ethers (XLVIII) (23). This mechanism predicts the photoproduct L obtained in the irradiation of γ -thujaplicin methyl ether (XLIX) (23).

The irradiation of purpurogallin tetramethyl ether (LI) in ethanol gives the photoproduct LII. The formation of the

Figure 6. Structures and reactions discussed in the historical section



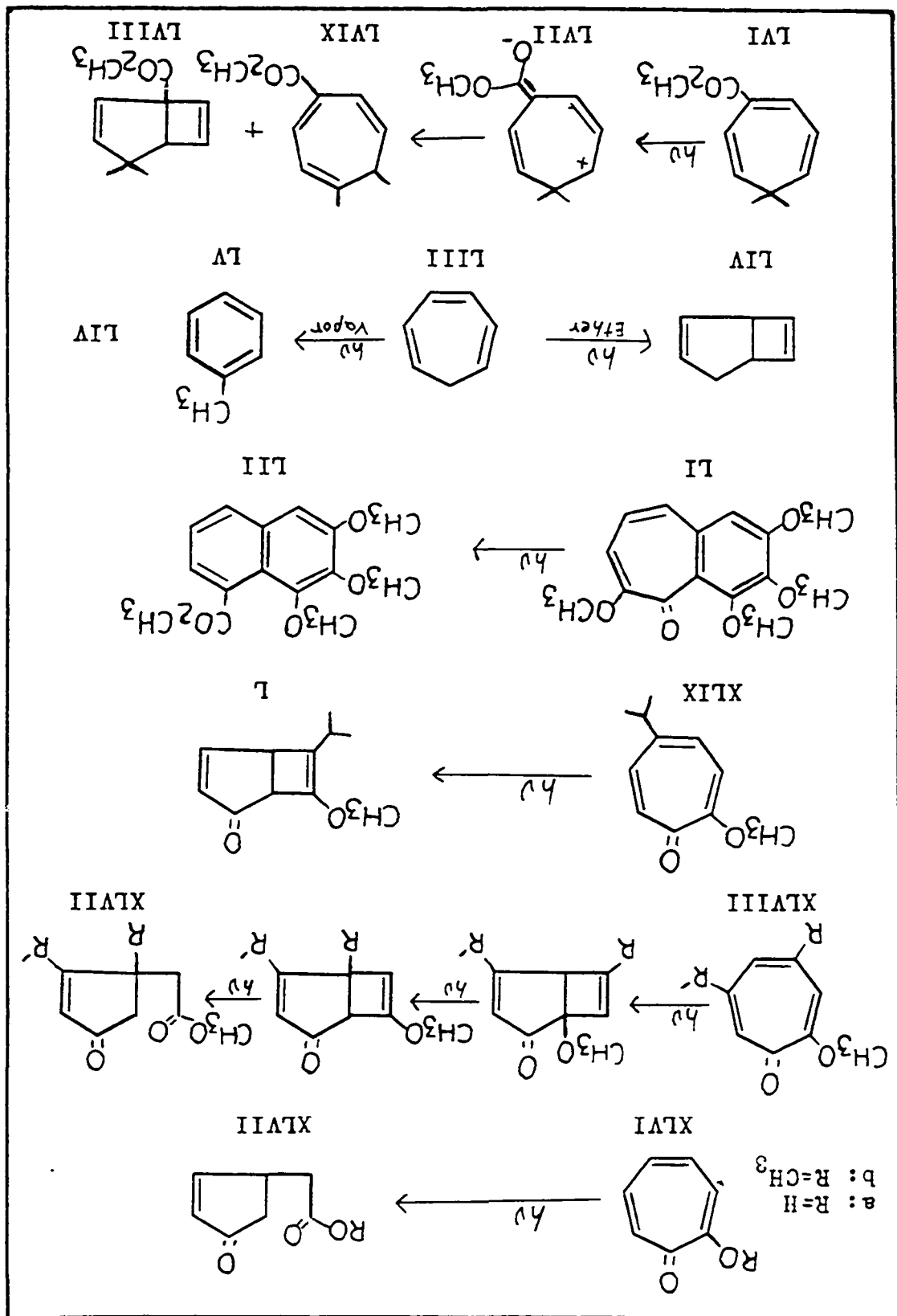
methyl ester in ethanol excludes a ketene as a possible intermediate. This reaction may proceed through a norcaradienone intermediate (24).

Cycloheptatrienes also give bicyclic photoisomers on irradiation in ether solutions. Irradiation of cycloheptatriene (LIII) in ether solution gives bicyclo [3.2.0] hepta-2,6-diene (LIV) (25,26).

In contrast, vapor phase irradiation gives toluene (LV) and the bicyclic product (26). The quantum yield for the formation of toluene increases with decreasing pressure, the extrapolated value at zero pressure being one within experimental error. This suggests that the photoisomerization of cycloheptatriene to toluene involves a vibrationally excited ground state while the photoisomerization to bicyclo [3.2.0] hepta-2,6-diene involves an electronically excited state (26).

Irradiation of methylthujate (LVI) in ether gives the bicyclic photoisomer LVIII and the rearranged product LVIX (27). It has been suggested that these products arise from the intermediate LVII (27).

Figure 7. Structures and reactions discussed in the historical section



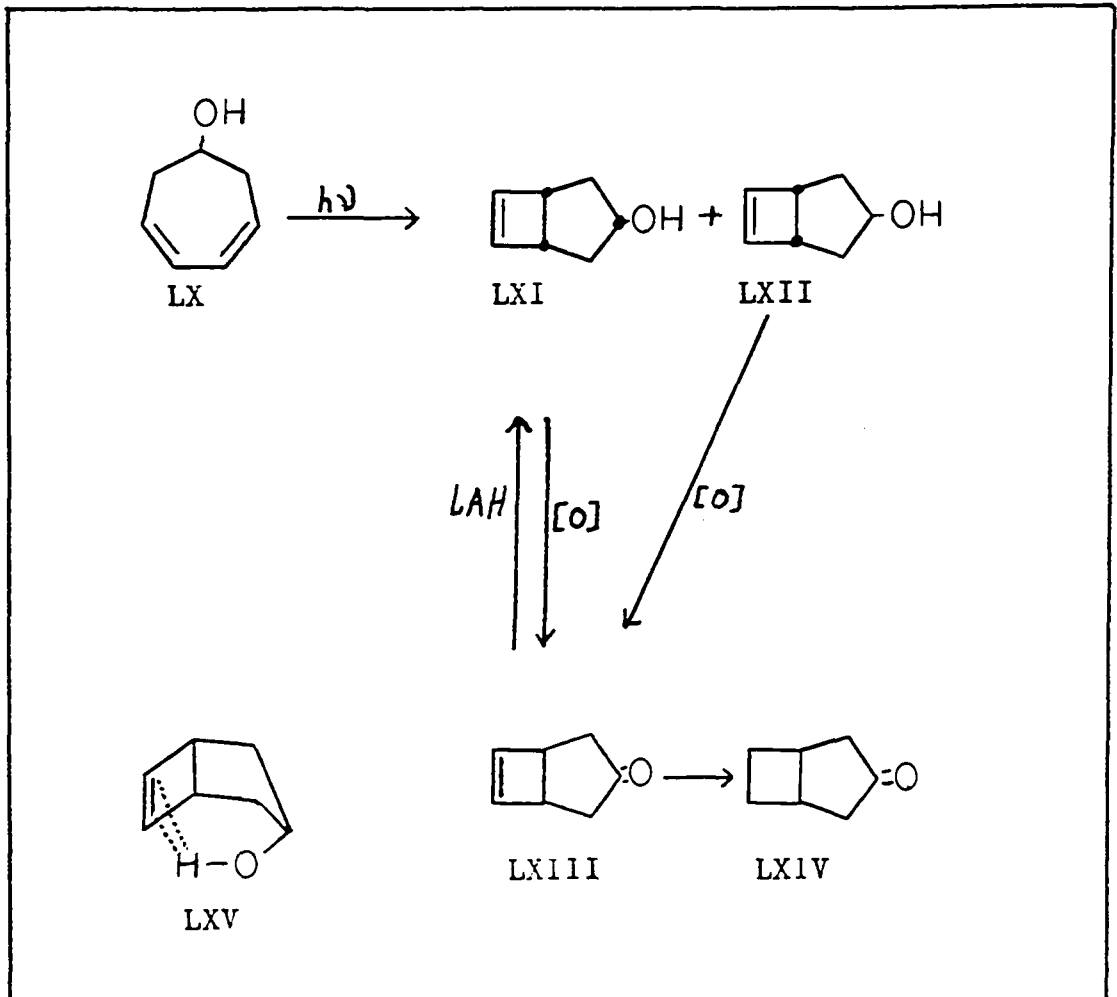
DISCUSSION

Photochemistry of Cycloheptadienols

1,3-cycloheptadiene (XXX) (12, 13) and 4-methoxy-3,5-cycloheptadienol (XXXII) (13) have been shown to give photo-products XXXI and XXXIV. Our interest in this facile synthetic route to bicycloheptanes led us to select 2,4-cycloheptadienol and 3,5-cycloheptadienol for this study. We considered the possibility of such a photoisomerization particularly intriguing because of the recently discovered route to a wide variety of substituted cycloheptadienes via 1,8-additions of Grignard reagents and metal hydrides to troponoid systems (28).

3,5-cycloheptadienol (LX) was prepared by the reaction of tropone with lithium aluminum hydride. Irradiation of LX in anhydrous ether gives the bicyclic photoisomers LXI and LXII in a 3:1 ratio. The mixture of photoisomers absorbed one equivalent of hydrogen over platinum. Separation of the photoisomers by preparative scale vapor phase chromatography gives LXI and LXII. The isomeric nature of LXI and LXII is established by oxidation to the same ketone LXIII. Similarly, oxidation of LXI and LXII individually gives the same ketone. Hydrogenation of LXIII gives the ketone LXIV which was compared directly and as the crystalline semicarbazone with an authentic sample of LXIV kindly provided by Dr. R. Srinivasan (29).

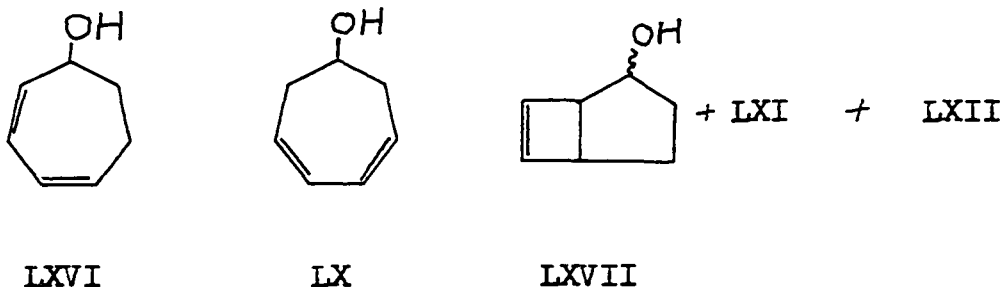
Figure 8. Equations illustrating the reactions of
3,5-cycloheptadienol (IX)



The stereochemistry of the alcohols LXI and LXII is assigned on the basis of the following evidence. Reduction of ketone LXIII with lithium aluminum hydride gives almost exclusively one alcohol which is identical with the major product of the irradiation. Attack by hydride on LXIII should take place predominately from the least hindered side of the bicyclic ketone and should lead to LXI. Strong indication that LXI is the endo-alcohol is provided by the vapor phase chromatographic retention time of LXI as compared with LXII. Alcohol LXI precedes LXII off the column by several minutes. This strongly suggests the hydrogen bonded structure LXV (30). The nuclear magnetic resonance spectrum of LXI supports this assignment. The olefinic protons of LXI appear at lower field (3.73 τ) than those reported for XXXI (4.24 τ), LXII (4.05 τ), LXIX (4.08 τ), or even LXIII (3.90 τ) consistent with an interaction between the cyclobutene double bond and the hydroxyl group which effectively removes electrons from the double bond.

A mixture of 3,5-cycloheptadienol (LX) and 2,4-cycloheptadienol (LXVI) was prepared by lithium aluminum hydride reduction of the 3,5-cycloheptadienone mixture obtained in the Hoffman degradation of tropinone methiodide (31). Irradiation of a mixture of alcohols LX and LXVI gives, after separation of the products by preparative scale vapor phase chromatography, the photoalcohols LXI and LXII and an isomeric alcohol formulated as LXVII on the basis of its nuclear magnetic resonance spectrum. The nuclear magnetic resonance

spectrum of LXVII shows two olefinic protons at 4.08 , two bridgehead protons as separate peaks at 6.04 τ and 7.00 τ . The C-2 proton at 6.77 τ , four methylene protons as a multiplet at 8.27 τ , and the hydroxyl proton at 7.96 τ . The generality of the



photoisomerization of 1,3-cycloheptadienes to bicyclo [3.2.0] heptenes coupled with the recently discovered synthesis of 1,3-cycloheptadienes (28) makes this photoisomerization an important synthetic entry to an otherwise difficulty available series of compounds.

Photochemistry of 3,5-Cycloheptadienone and 2-Methyl-3,5-Cycloheptadienone

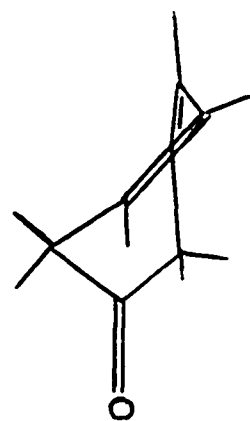
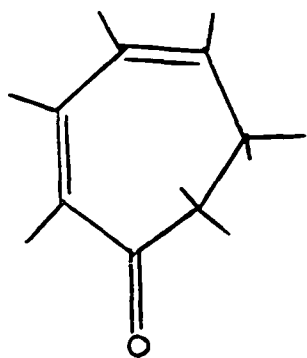
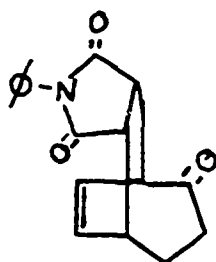
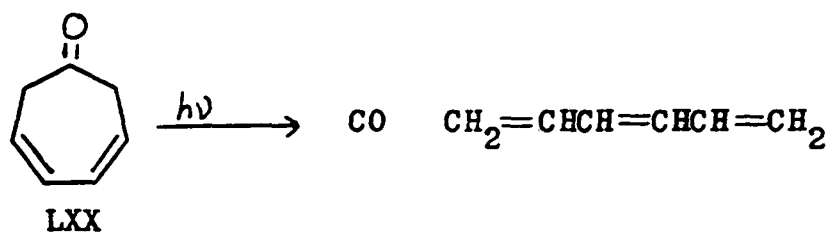
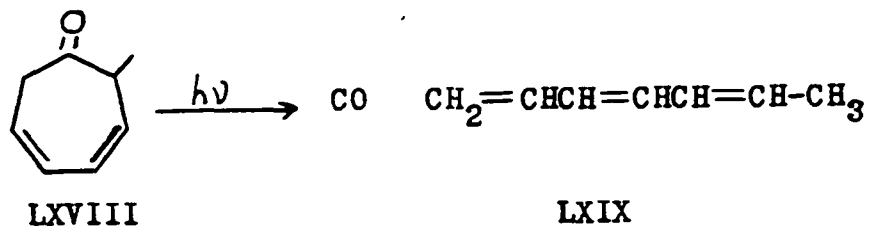
The photochemical behavior of 2-methyl-3,5-cycloheptadienone (LXVIII) and 3,5-cycloheptadienone (LXX) presents a surprising contrast to the normal cyclization of other conjugated cycloheptadienes to bicyclo [3.2.0] heptenes. Irradiation of 2-methyl-3,5-cycloheptadienone (LXVIII) in ether gives carbon monoxide (95%), collected in a gas cell and identified by its infrared spectrum, and a mixture of geometric isomers of 1,3,5-heptatriene (LXIX, 252,261, and 271 μ) which analyzes for C_7H_{10} . LXIX absorbed three equivalents of hydrogen over

platinum and the product was identified as n-heptane. In a similar fashion irradiation of 3,5-cycloheptadienone (LXX) gives a mixture of isomeric 1,3,5-hexatrienes (LXXI, 246, 256, and 266 m μ) (32). These reactions proceed smoothly in pyrex vessels which suggests that the reaction is initiated by excitation of the $n \rightarrow \pi^*$ transition of the carbonyl group.* The excitation of the low wave length chromophore and the $n \rightarrow \pi^*$ transition of LXVIII and LXX by irradiation in quartz vessels produces no detectable valence tautomerization.

An examination of the unusual physical and chemical properties of 3,5-cycloheptadienones suggest a possible rationalization of these anomalous photochemical reactions. Meinwald et al. showed that attempts to form a Diels-Alder adduct of 3,5-cycloheptadienone (LXX) give the isomerized product LXXII (31). The anomalous properties of 3,5-cycloheptadienones must be due to the steric problems in this arrangement of trigonal atoms in the seven-membered ring. Examination of Dreiding models shows that 2,4-cycloheptadienone can easily assume a configuration in which all trigonal atoms are essentially planar but 3,5-cycloheptadienone has the diene chromophore badly distorted. It is not surprising that the molecule shows properties more like a non-conjugated than a conjugated diene.

*It is possible that intramolecular energy transfer occurs between the excited carbonyl and diene system. This would be analogous to the intermolecular transfer of energy from the low lying triplet state of benzophenone to acyclic dienes (33).

Figure 9. Structures and reactions discussed in the photochemistry of 3,5-cycloheptadienone



This also suggests a rationalization of the anomalously low wave length ultraviolet absorption of 3,5-cycloheptadienone (214 mu) (31) and 2-methyl-3,5-cycloheptadienone (217 mu) (28). Many β,γ -unsaturated ketones show ultraviolet absorption in the 210-220 mu region due to $\pi\rightarrow\pi^*$ transitions involving the non-conjugated double bond and the carbonyl group. A similar interaction may occur in the 3,5-cycloheptadienones offering an explanation of the anomalous ultraviolet absorption of these compounds.* These dienes do not undergo the light-induced valence tautomerizations common to other conjugated cycloheptadienes because they lack the characteristic diene chromophore.

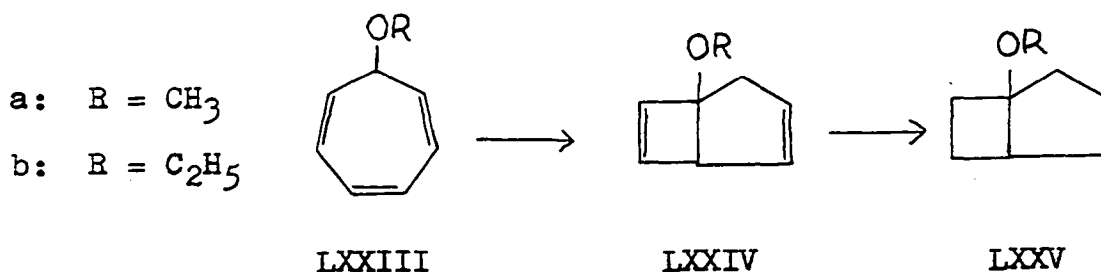
Photochemistry of 7-Alkoxy-1,3,5-Cycloheptatrienes
and 1-Alkoxy-1,3,5-Cycloheptatrienes

The irradiation of tropolone ethers, (17,20,23,34,35) 1,3-cycloheptadienes, (12,13,14,36) cycloheptatriene, (13,26) and methyl 5,5-dimethyl-1,3,6-cycloheptatrienecarboxylate (27) in solution gives in each case a bicyclic valence tautomer without skeletal rearrangement. In fact, this type of transformation is among the most general and useful photochemical rearrangements. Irradiation of cycloheptatriene in the vapor phase gives primarily toluene (26). Irradiation of

*Reduction of the carbonyl group to an alcohol relieves most of the strain inherent in the 3,5-cycloheptadienone and the diene system becomes normal (λ max. 241 mu; and gives a normal Diels-Alder adduct.) (31).

7-alkoxycycloheptatrienes is, in contrast, anomalous both in solution and in the vapor phase. Irradiation of 7-methoxy-1,3,5-cycloheptatriene (LXXIIIa) in ether gives a bicyclic photoisomer formulated as LXXIVa. Similarly, irradiation of 7-ethoxy-1,3,5-cycloheptatriene (LXXIIIb) gives the corresponding bicyclic product LXXIVb.

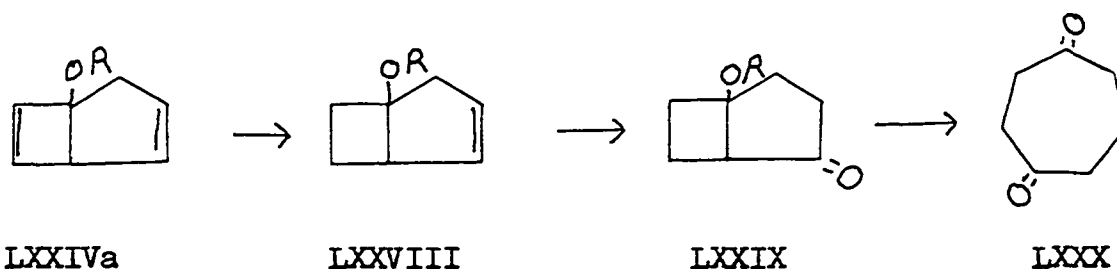
The structure of LXXIVa,b is based on the following evidence. The photoisomers show no intense ultraviolet absorption above 220 μ . The nuclear magnetic resonance spectra shows LXXIVa: (cyclobutene protons, 3.80 τ ; cyclopentene protons, 4.13 τ ; bridgehead proton, 6.46 τ ; methoxyl protons, 6.76 τ ; and allylic methylene protons, 7.62 τ), LXXIVb; (cyclobutene protons, 3.77 τ ; cyclopentene protons, 4.30 τ ; bridgehead proton, 6.46 τ ; ethyl methylene protons, 6.56 τ ; allylic methylene protons, 7.55 τ ; and methyl protons, 8.88 τ). LXXIVa and LXXIVb absorb two equivalents of hydrogen over platinum giving LXXVa and LXXVb which do not show any proton resonance characteristic of the -CH-OR grouping.



Pyrolysis of the bicyclic products LXXIVa and LXXIVb gives the corresponding 1-alkoxy-1,3,5-cycloheptatrienes (LXXVIa and LXXVIb) which were identified by direct comparison with

(cyclopentene protons, 4.30).

Hydroboration of LXXVIIIa followed without isolation by oxidation with aqueous chromic acid (38) gives tetrahydrophoto- - tropolone methyl ether LXXIXa which is converted very rapidly in acid to 1,4-cycloheptanedione (LXXX) (20). The 1,4-cycloheptanedione thus obtained was compared as the bis-2,4-dinitrophenylhydrazone with an authentic sample (20,39).



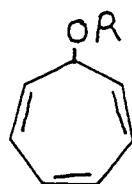
A second ketone expected in the oxidation was not isolated.

Irradiation of a mixture of 7-ethoxy-1,3,5-cycloheptatriene (LXXIIIb) and benzophenone in a Pyrex vessel gives a 21% conversion to the bicyclic product LXXIVb. This would suggest an intermolecular energy transfer from the low lying triplet state of benzophenone to the cycloheptatriene analogous to the transfer between benzophenone and acyclic dienes (33) since Pyrex does not transmit in the absorption range of LXXIIIb.

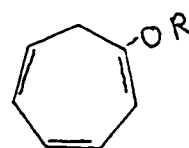
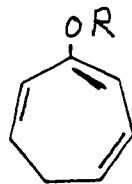
Irradiation of LXXIIIa in the vapor phase gives starting material (14%) 1-methoxy-1,3,5-cycloheptatriene (38%) and 1-methoxybicyclo 3.2.0 hepta-3,6-diene. Vapor phase chromatographic analysis of the product failed to detect any toluene derivatives analogous to those obtained in the vapor phase irradiation of cycloheptatriene (26). Photo-

chemical rearrangements of LXXIIIa,b and LXXVIa,b to LXXIVa,b pose several interesting problems in interpretation. It seems reasonable in view of the results of the vapor phase irradiation of LXXIIIa and the low yield obtained in the irradiation of 1-alkoxy-1,3,5-cycloheptatriene in solution to assume that the rearranged bicyclic photoisomer (LXXIVa) is formed from an excited state of 1-methoxy-1,3,5-cycloheptatriene. The results of the sensitized irradiation of LXXIIIb suggest that at least the first step involves a triplet state. The occurrence of both LXXVIa and LXXIVa in the vapor phase irradiation suggests that collisional loss of excess vibrational energy is stabilizing the bicyclic product more efficiently in solution than in the vapor phase. The conversion of LXXVIa,b to LXXIVa,b may be viewed as a normal photochemical cyclization.

The photochemical rearrangement of LXXIIIa,b to LXXIVa,b is at least formally analogous to the thermal isomerization of 7-deuterio-1,3,5-cycloheptatriene (40) and could be viewed as a result of two successive transannular hydrogen transfer processes. An alternate explanation is that LXXIIIa,b may

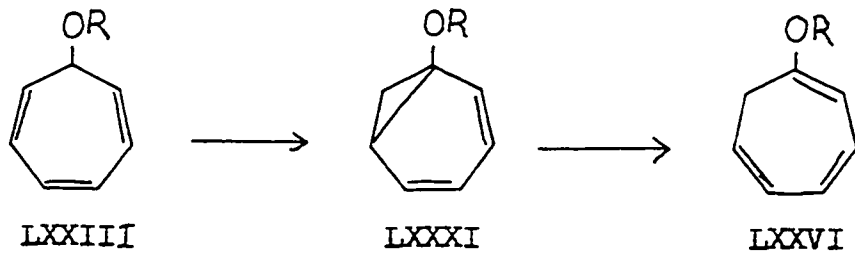


LXXIII



LXXVI

undergo a light-induced hydrogen shift leading to LXXXI, the norcaradiene tautomer of LXXVI.



Photochemistry of 1,3,5-Cyclooctatriene

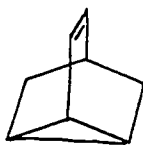
Reflection on the possible photochemical transformations of cyclooctadienes and trienes suggest that two modes of reactions are possible, valence tautomerization and ring cleavage. In the case of 1,3-cyclooctadiene this would lead to either hexatriene and ethylene or bicyclo [4.2.0] oct-7-ene (25). Irradiation of 1,3-cyclooctadiene (LXXXII) gives the bicyclic tautomer (LXXXIII) (25,41). Photosensitized irradiation of 1,5-cyclooctadiene (LXXXIV) gives the tricyclic product LXXXV (42). Similarly, irradiation of 2,4,6-cyclooctatrienone (LXXXVI) in nonpolar solvents gives LXXXVII (43); irradiation of LXXXVI in methanol gives methyl 2,4,6-octatrienoate (LXXXVIII) (43).

Investigation of the photochemistry of cycloheptatrienes led naturally to an interest in the photochemistry of 1,3,5-cyclooctatriene. Irradiation of 1,3,5-cyclooctatriene (LXXXIX) in anhydrous ether gives after distillation and separation of the volatile components by vapor phase chromatography XC (48%), XCI (38%), and XCII (14%). The overall yield of volatile components is 41%. XC was identified by comparison with a known sample of 1,5-cyclooctadiene. It was not possible to determine whether the 1,5-cyclooctadiene was present in the starting material as previously reported (44) or was produced by a photoreduction process.

The structure of XCI is based on the following evidence.

Reduction of XCI with two equivalents of hydrogen gives XCIII, identical with a sample prepared by the hydrogenation of LXXXIII. The nuclear magnetic resonance spectrum of XCI shows cyclobutene protons, 3.91 τ ; cyclohexene protons, 4.27 τ ; bridge-head protons, 6.85 τ ; allylic methylene protons, 8.17 τ ; and methylene protons, 8.33 τ consistent with structure XCI.

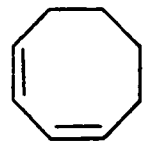
The structure of XCII is based on the following evidence. Reduction of XCII with one equivalent of hydrogen gives a compound (XCIV) with no nuclear magnetic resonance or infrared absorption characteristic of carbon-carbon unsaturation. Molecular weights found for XCII and XCIV are 111 and 114 respectively. The above data and correct analysis for C_8H_{10} establishes the tricyclic character of XCII. The ultraviolet spectrum shows an intense absorption (shoulder) at 208 $m\mu$ (5300) suggesting the presence of a vinyl cyclopropane chromophore. The nuclear magnetic resonance spectrum shows a two-proton multiplet at approximately 4.67 τ , a one-proton multiplet at 7.00 τ , a one-proton multiplet at 7.62 τ , and a six-proton multiplet centered at approximately 8.35 τ . The above facts are consistent with the previously proposed structure XCV.



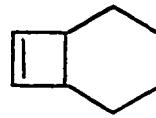
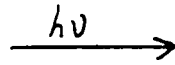
XCV

The vinyl proton coupling (6.0 \pm 1 c.p.s.) of the photoisomer, however, suggests (45)

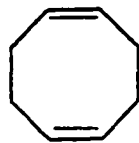
Figure 10. Structures and reactions discussed in the photochemistry of 1,3,5-cyclooctatriene



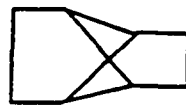
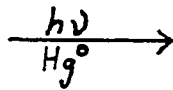
LXXXII



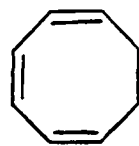
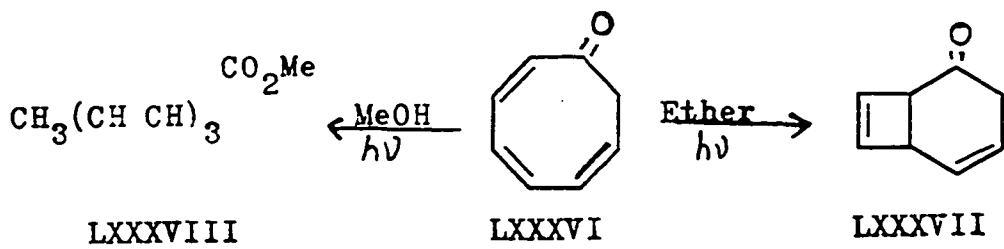
LXXXIII



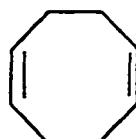
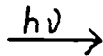
LXXXIV



LXXXV

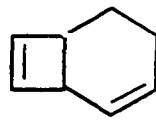


LXXXIX



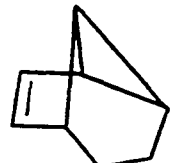
XC

+

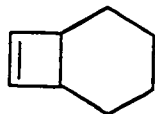


XCI

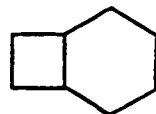
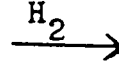
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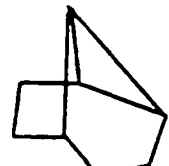
XCII



LXXXIII



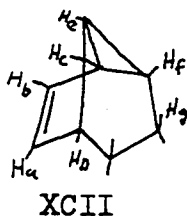
XCIII



XCIV

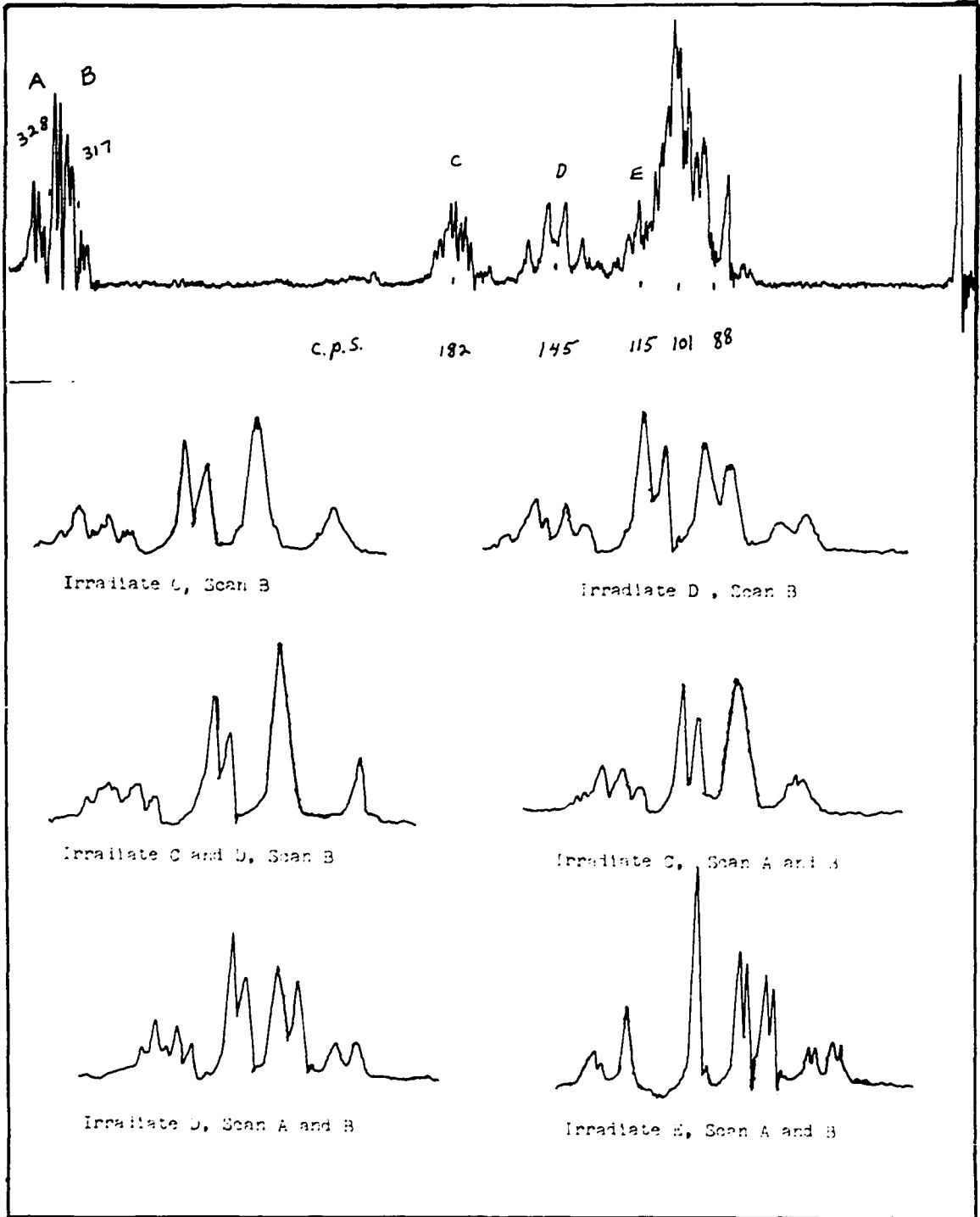
that the olefinic bond is in a five rather than a six-membered ring. To explore this possibility the hydrocarbon XCIV was compared with a sample of XCV kindly provided by Professor N. Le Bel. XCV was shown to be nonidentical with XCIV by comparison of vapor phase chromatographic retention times. The above data limits the possible structures which could be assigned to XCII. The structure of XCI is conclusively established by spin decoupling experiments. These spectra are shown in Figure 11.

The spin decoupling experiments show that the lower field olefinic proton is strongly coupled to a proton at approximately 8.1τ , the upper field olefinic proton is strongly coupled to the proton absorbing at 7.00τ , the proton absorbing at 7.6τ is coupled to a proton or protons in the high field multiplet, and the proton absorbing at 7.6τ is not coupled to the olefinic protons. These facts are consistent with the structure XCII. Proton assignments may be made as follows:



vinyl protons H_a and H_b, 4.7τ and 4.5τ ; bridgehead proton H_c, 8.1τ ; bridgehead proton H_d, 6.96τ ; and protons H_e and H_f in the high field absorption. The proton absorbing at 7.6τ is probably the exo-methylene proton H_g. Structure XCI is in accord with the observed vinyl proton coupling (6.0 ± 1 c.p.s.).

Figure 11. Illustration of the spin decoupling experiment
of tricyclo[5.1.0.0^{4,8}]oct-2-ene (XCII)

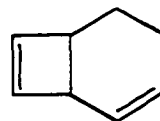


The conversion of LXXXIX to XCI and XCII does not involve skeletal rearrangement in either case and may be viewed as a valence tautomerization.

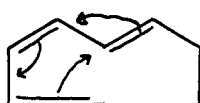


LXXXIX

|||



XCI



LXXXIX



XCII

Figure 12. Nuclear magnetic resonance spectra

top: endo-Bicyclo[3.2.0]hept-6-en-3-ol (LXI)

bottom: exo-Bicyclo[3.2.0]hept-6-en-3-ol
(LXII)

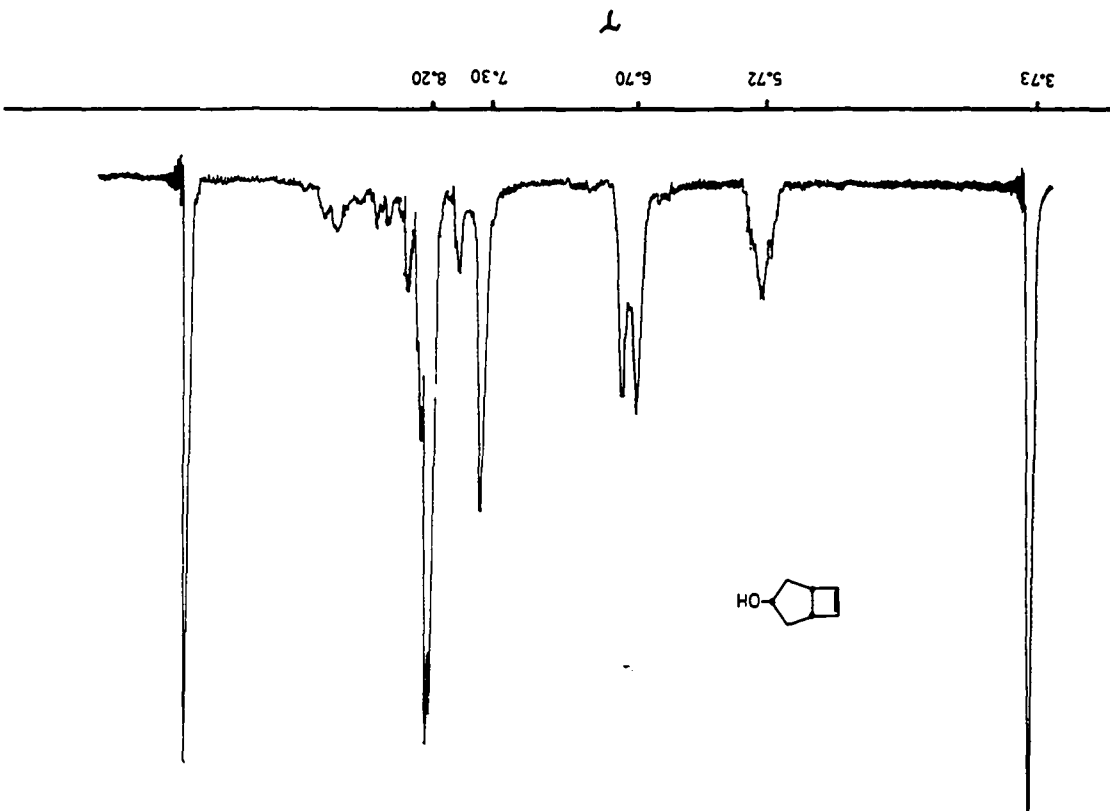
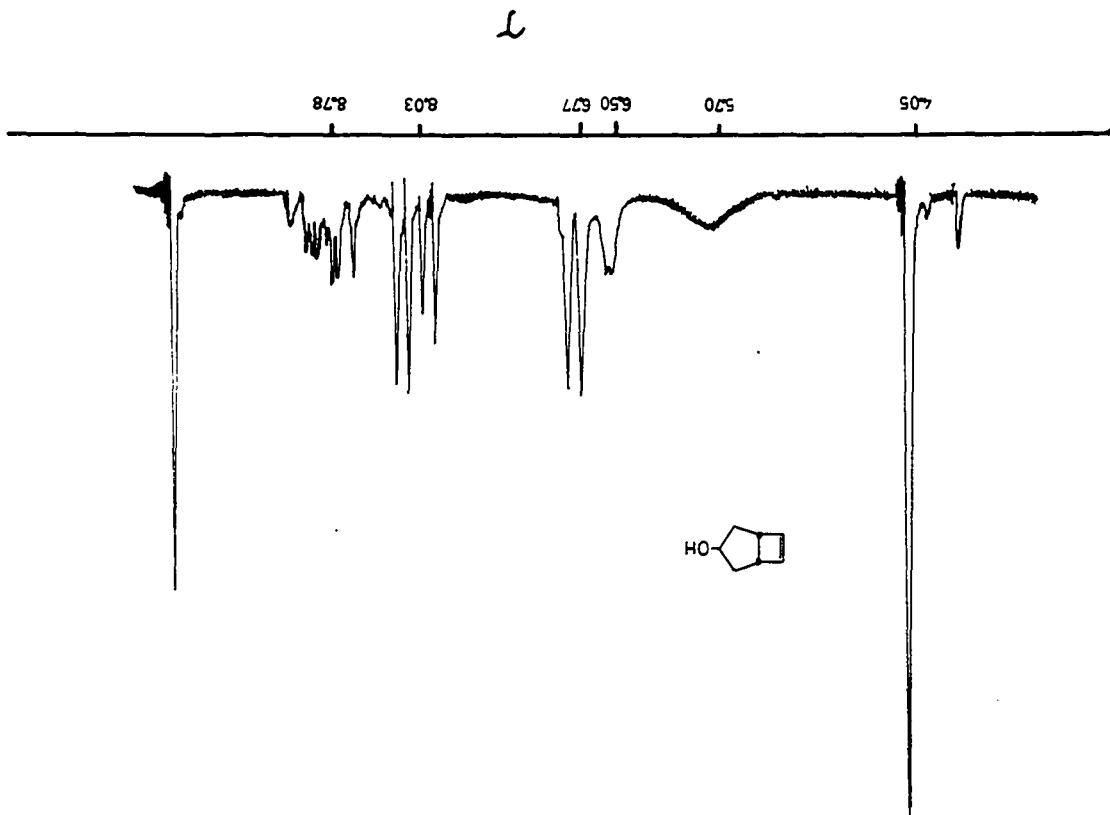


Figure 13. Nuclear magnetic resonance spectra

top: Bicyclo[3.2.0]hept-6-en-2-ol (LXVII)

bottom: Bicyclo[3.2.0]hept-6-en-3-one (LXIII)

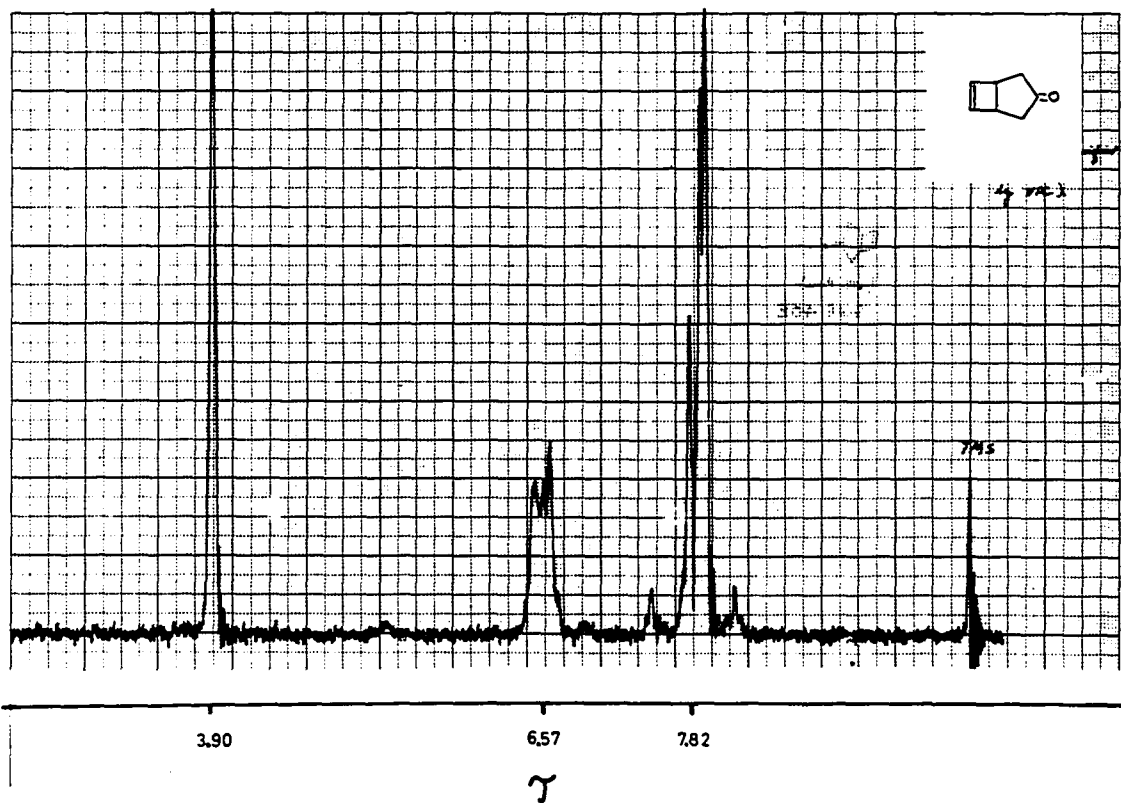
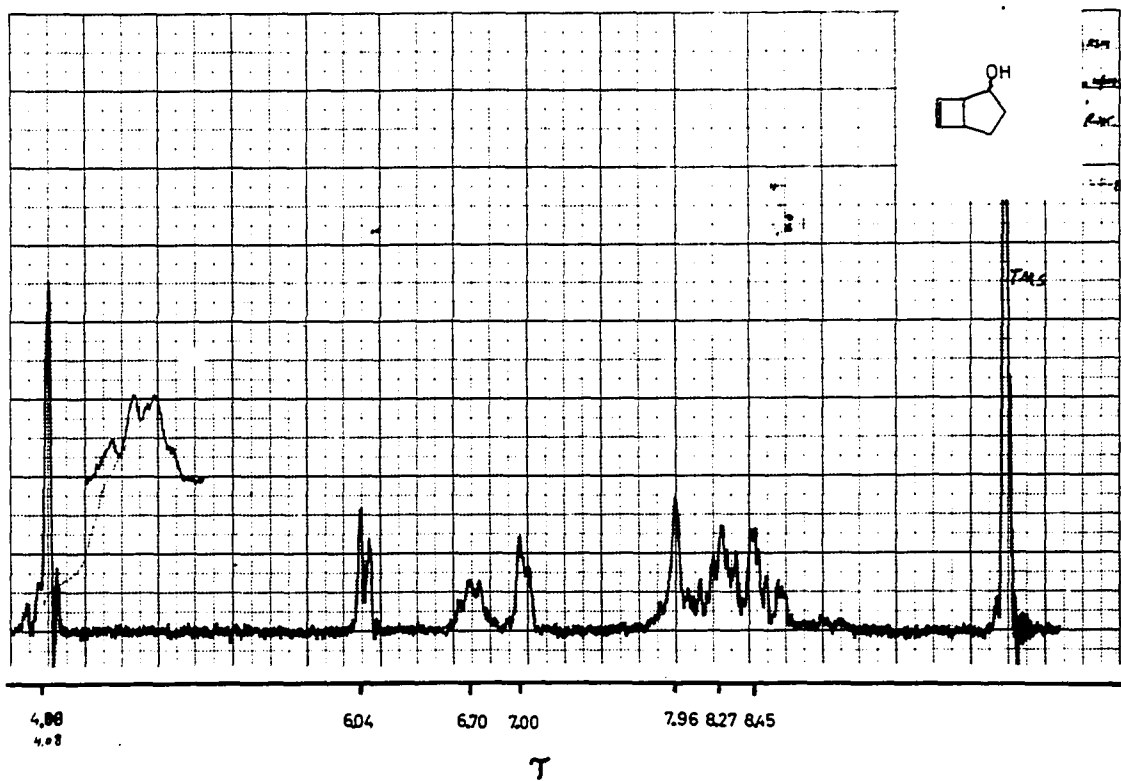


Figure 14. Infrared spectra

top: endo-Bicyclo[3.2.0]hept-6-en-3-ol (LXI)

middle: exo-Bicyclo[3.2.0]hept-6-en-3-ol (LXII)

bottom: Bicyclo[3.2.0]hept-6-en-3-one (LXIII)

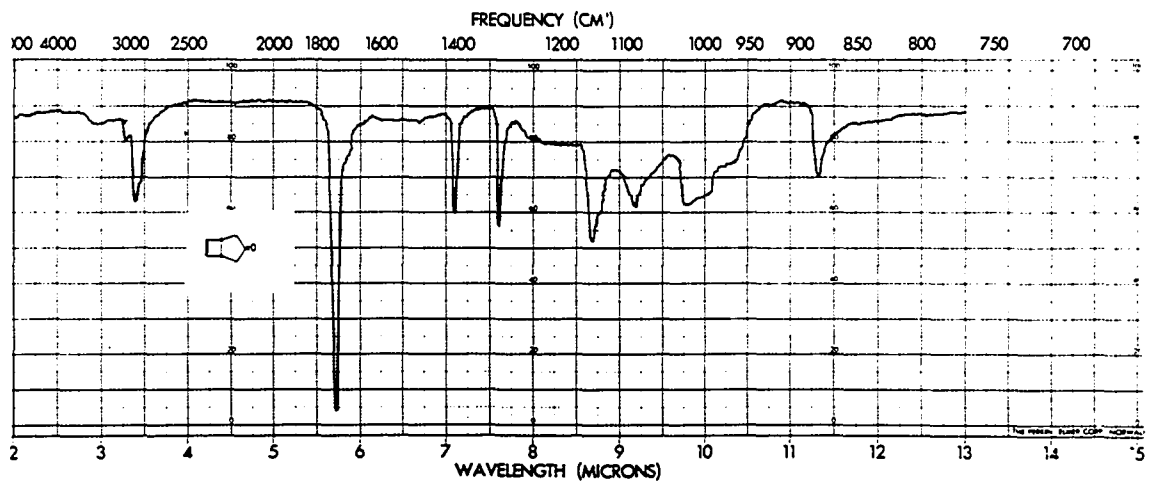
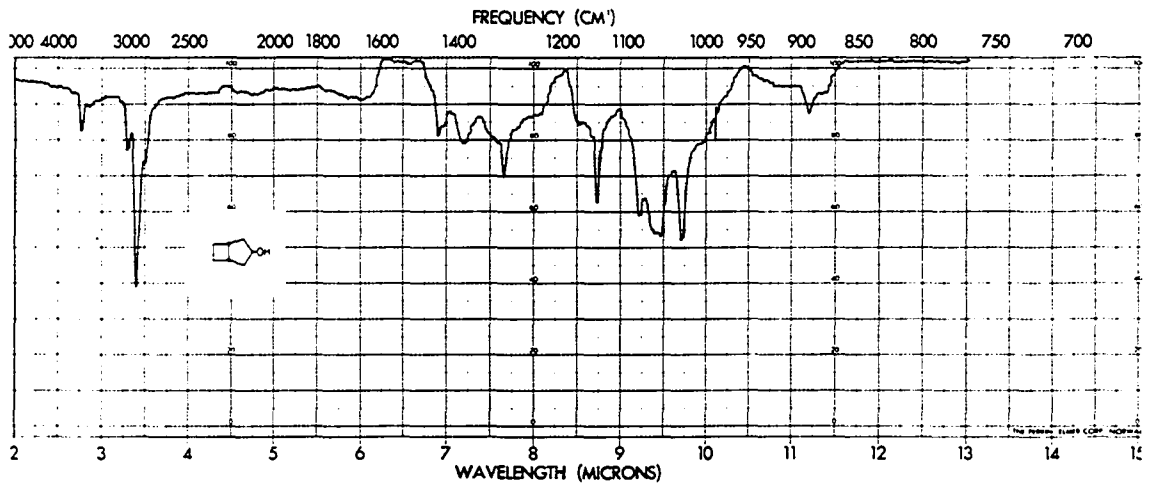
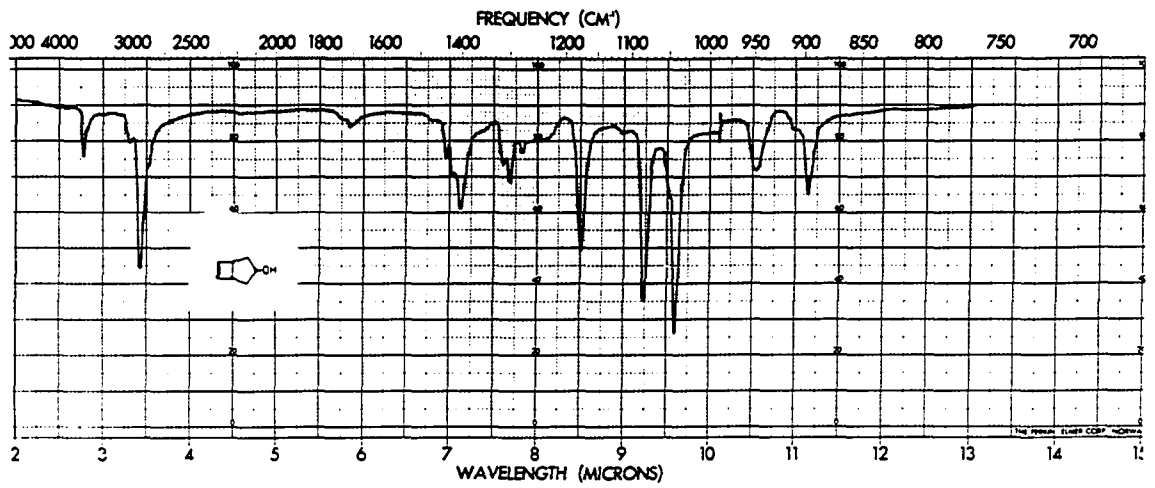


Figure 15. Infrared spectra

top: semicarbazone of Bicyclo[3.2.0]hept-*n*-3-one (LXIV)

bottom: Bicyclo [3.2.0] Hept-6-en-2-ol (LXVII)

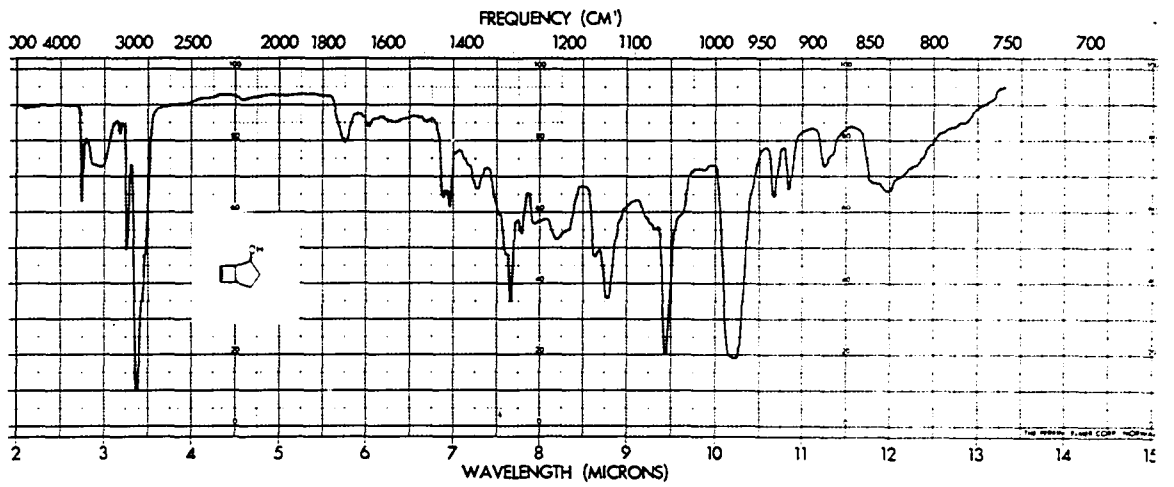
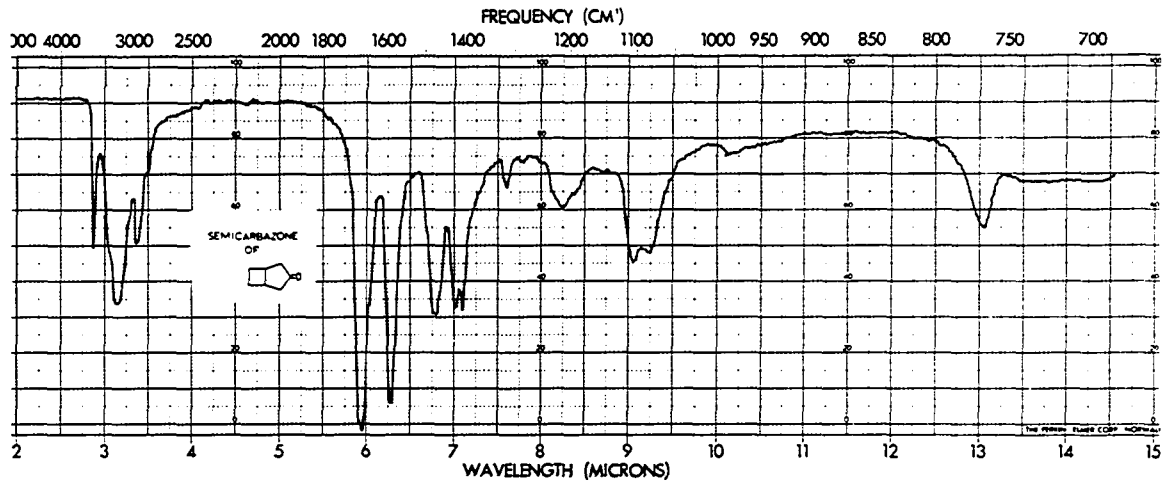


Figure 16. Infrared spectra

top: 1,3,5-Hexatriene (LXXI)

bottom: 1,3,5-Heptatriene (LXIX)

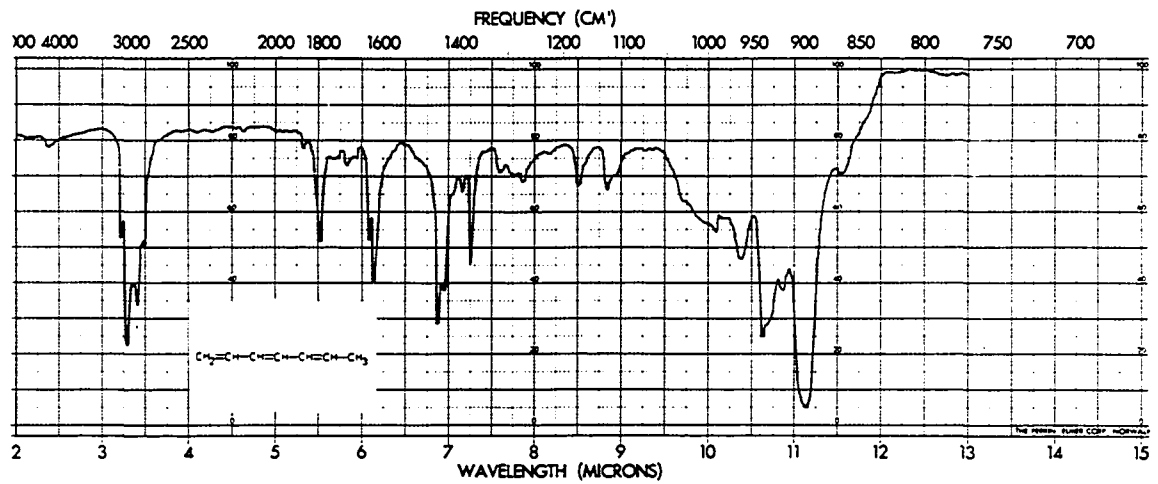
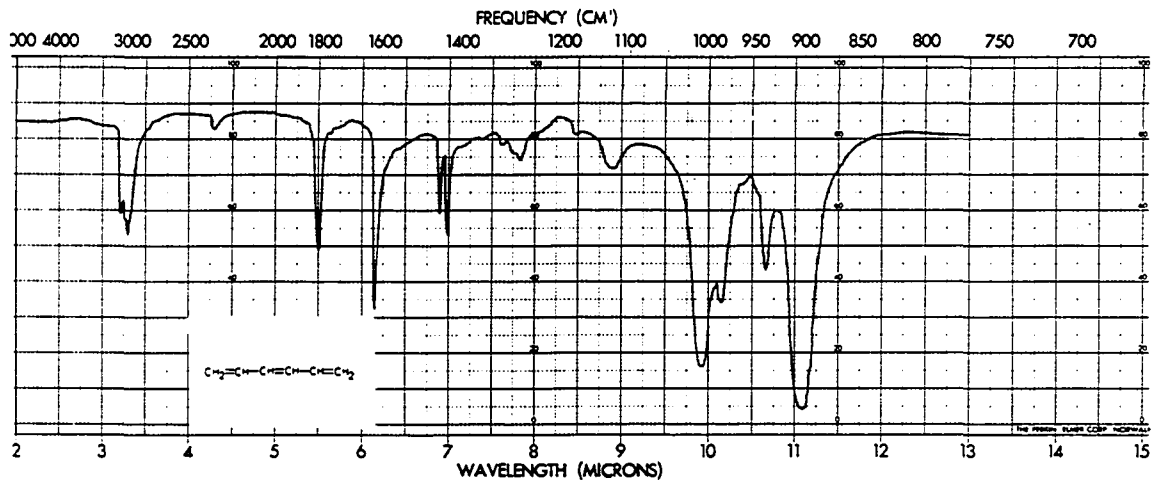


Figure 17. Nuclear magnetic resonance spectra

top: 7-Methoxy-1,3,5-cycloheptatriene
(LXXIIIa)

bottom: 7-Ethoxy-1,3,5-cycloheptatriene
(LXXIIIb)

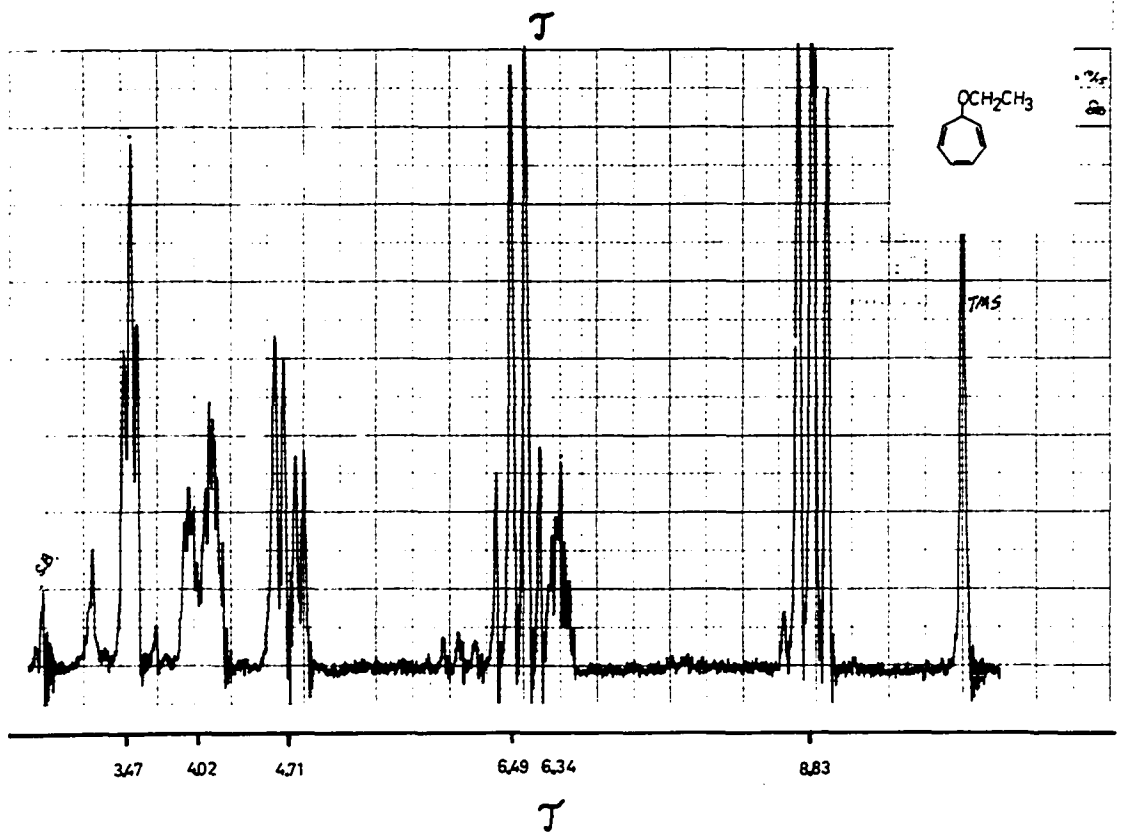
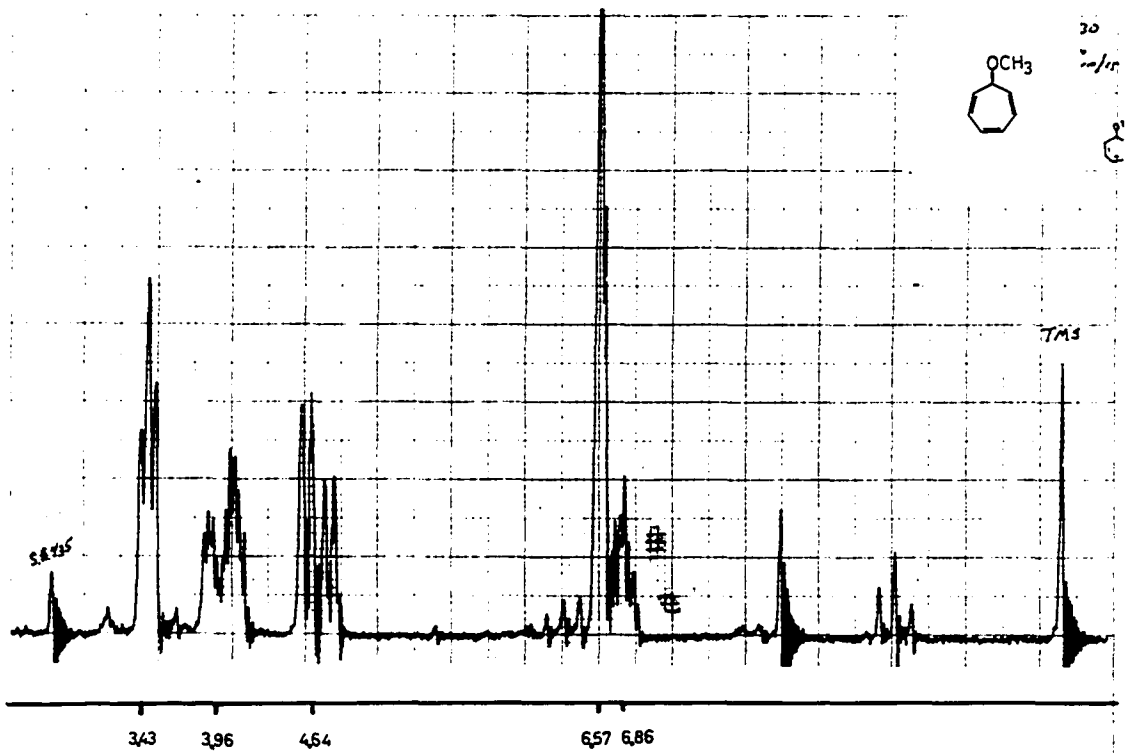


Figure 18. Nuclear magnetic resonance spectra

top: 1-Methoxy-1,3,5-cycloheptatriene (LXXVIa)

bottom: 1-Ethoxy-1,3,5-cycloheptatriene
(LXXVIb)

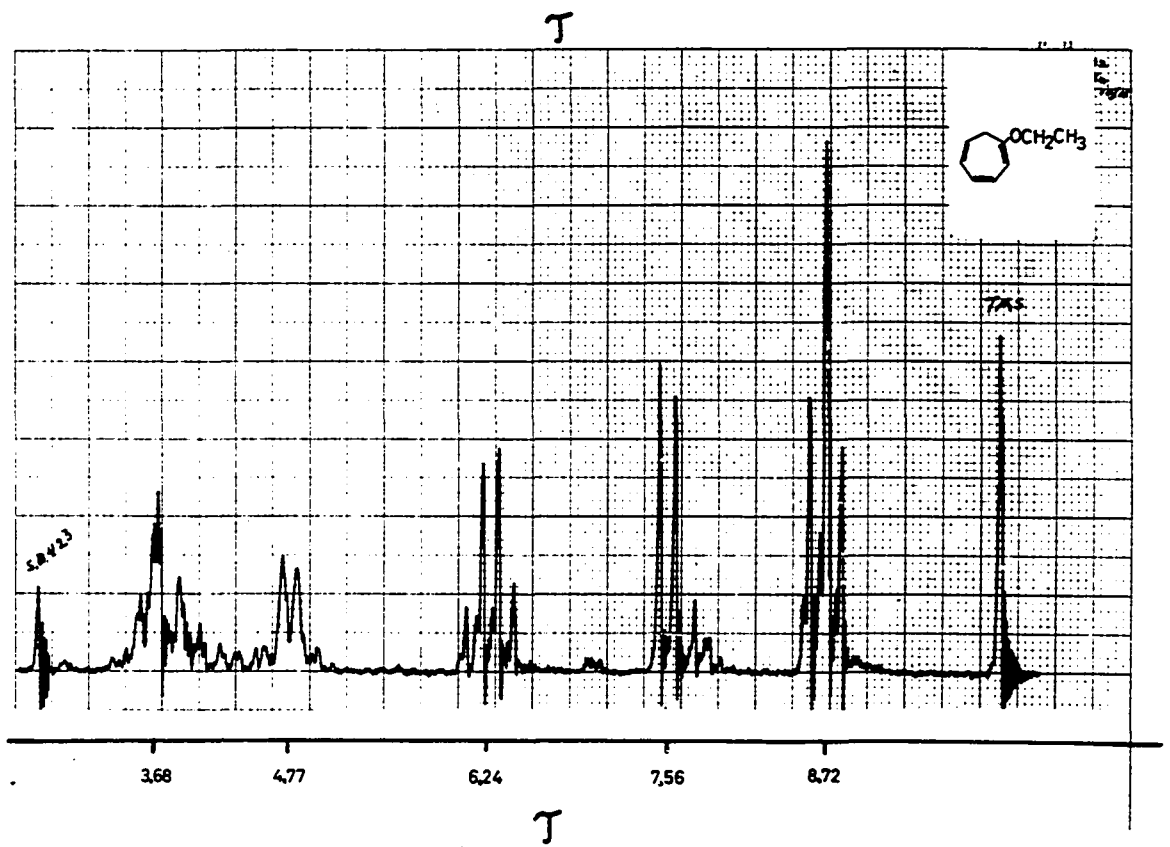
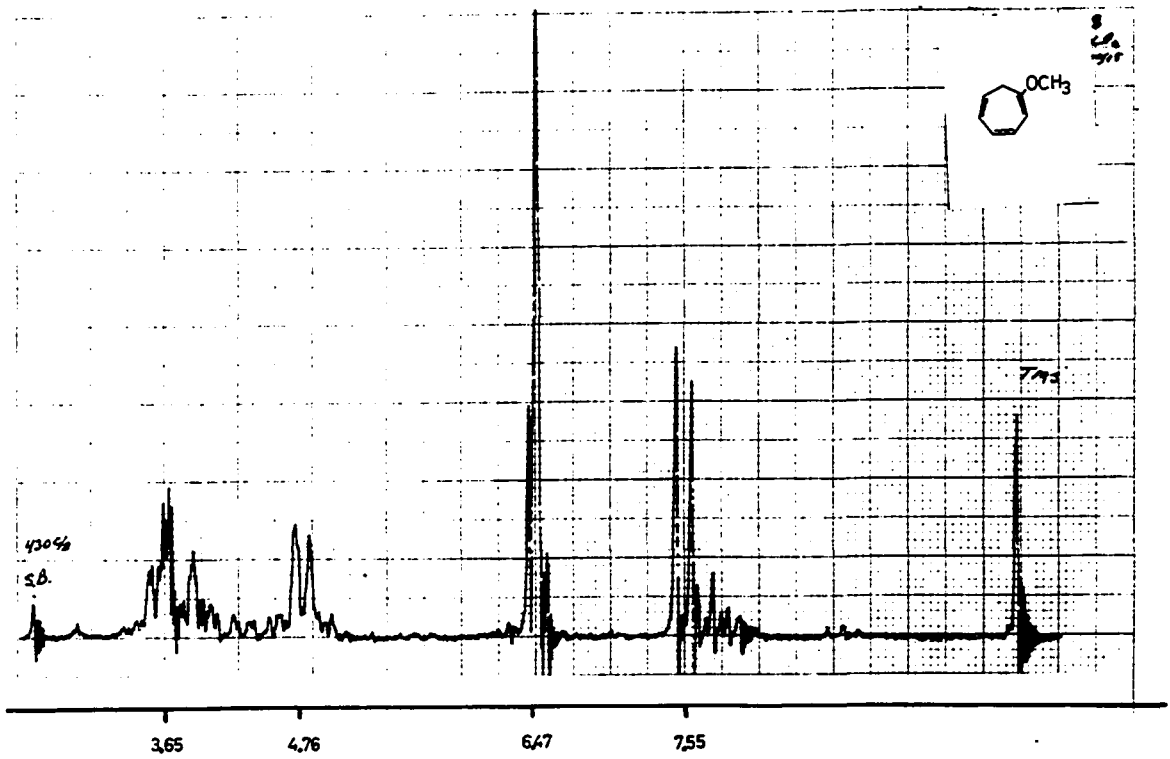


Figure 19. Nuclear magnetic resonance spectra

top: 1-Methoxybicyclo [3.2.0] hepta-3,6-diene
(LXXIVa)

bottom: 1-Ethoxybicyclo [3.2.0] hepta-3,6-
diene (LXXIVb)

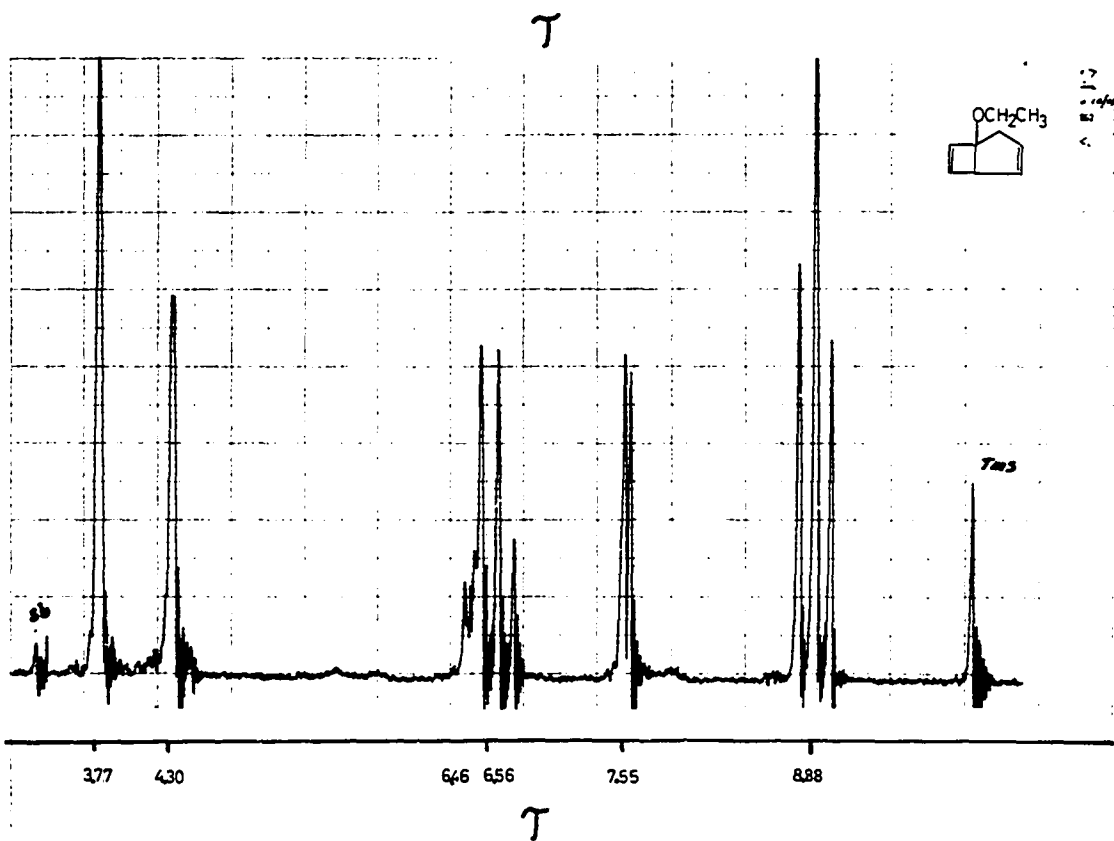
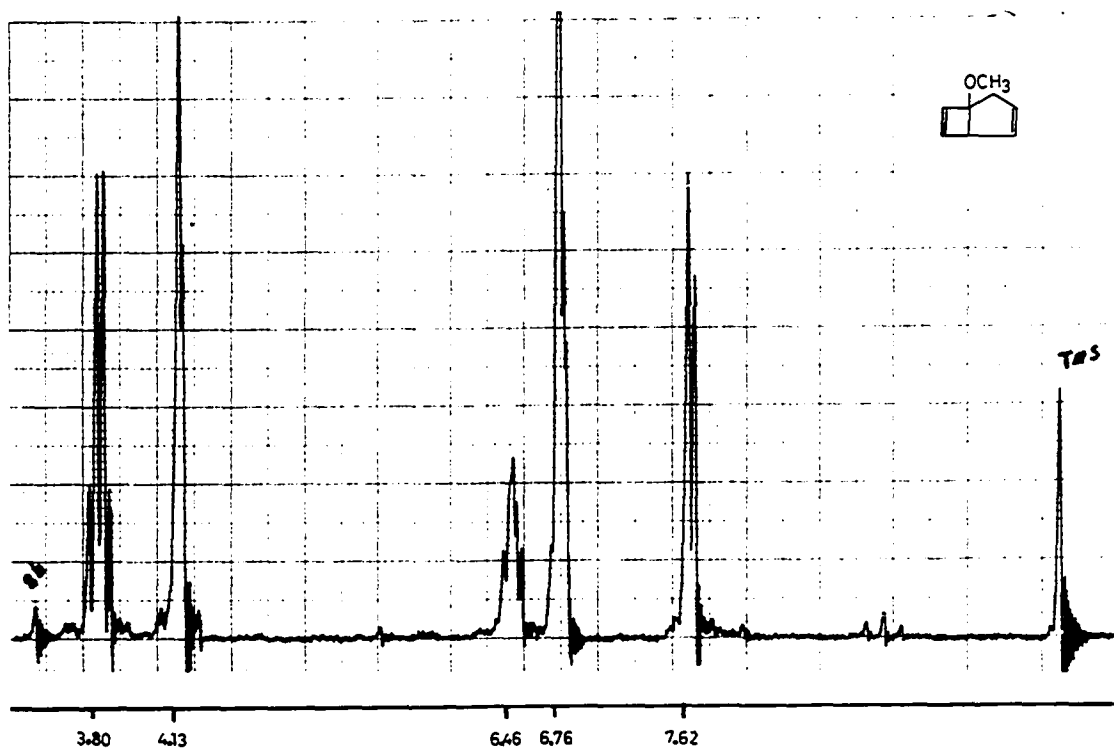


Figure 20. Nuclear magnetic resonance spectra

top: 1-Methoxybicyclo [3.2.0] heptane (LXXVa)

bottom: 1-Ethoxybicyclo [3.2.0] heptane
(LXXVb)

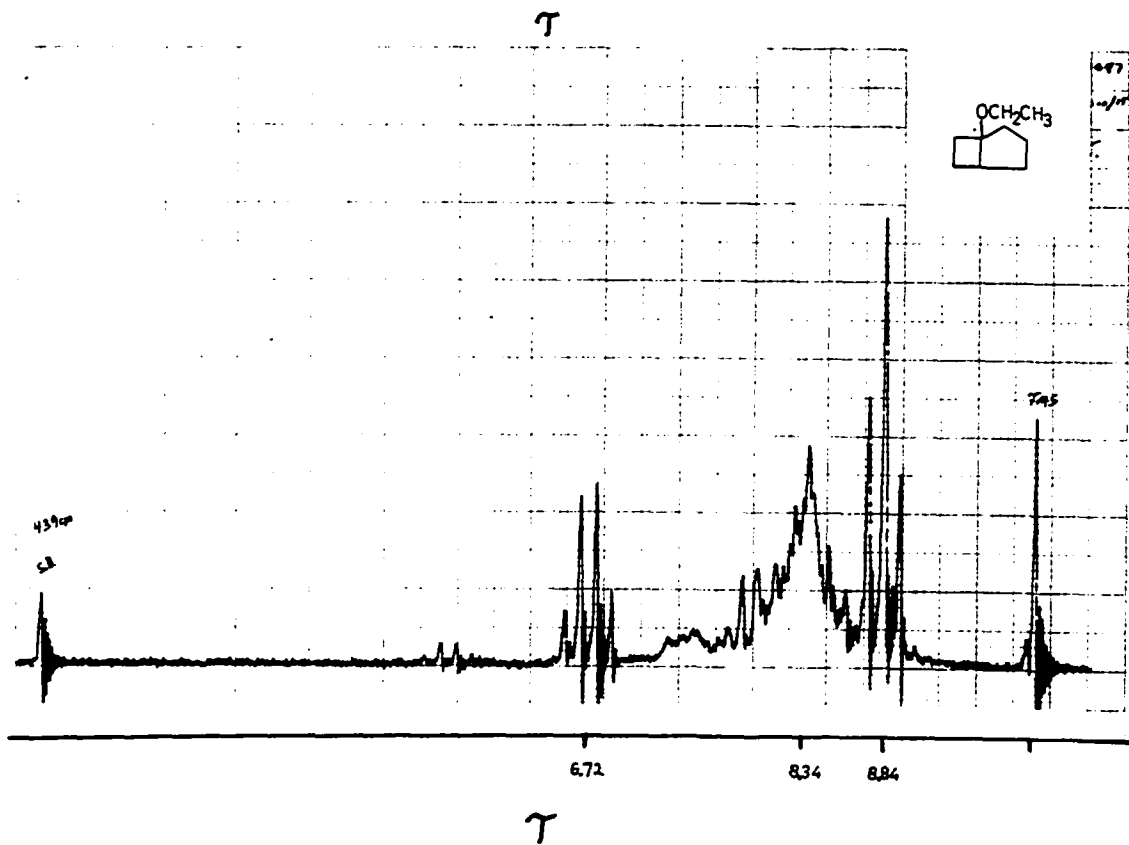
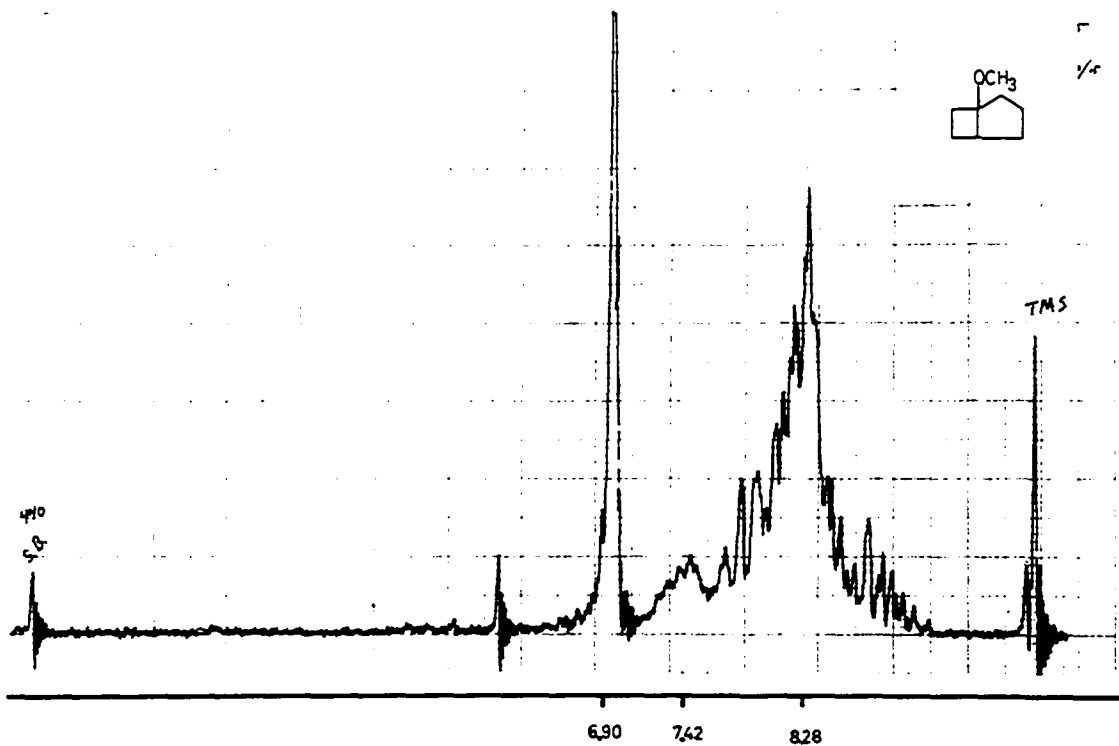


Figure 21. Infrared spectra

top: 7-Methoxy-1,3,5-cycloheptatriene
(LXXIIIa)

middle: 7-Ethoxy-1,3,5-cycloheptatriene
(LXXIIIb)

bottom: 1-Methoxy-1,3,5-cycloheptatriene
(LXXVIa)

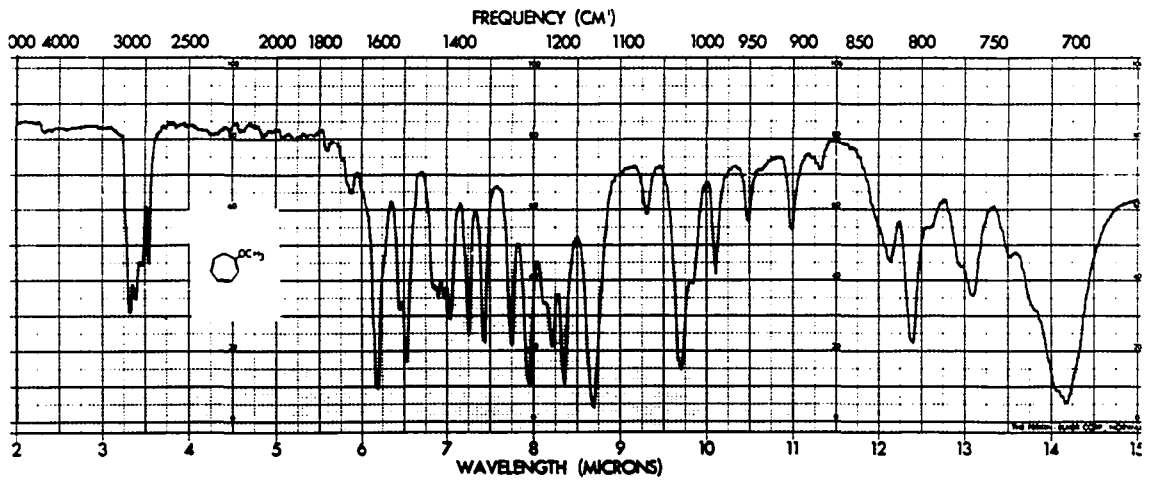
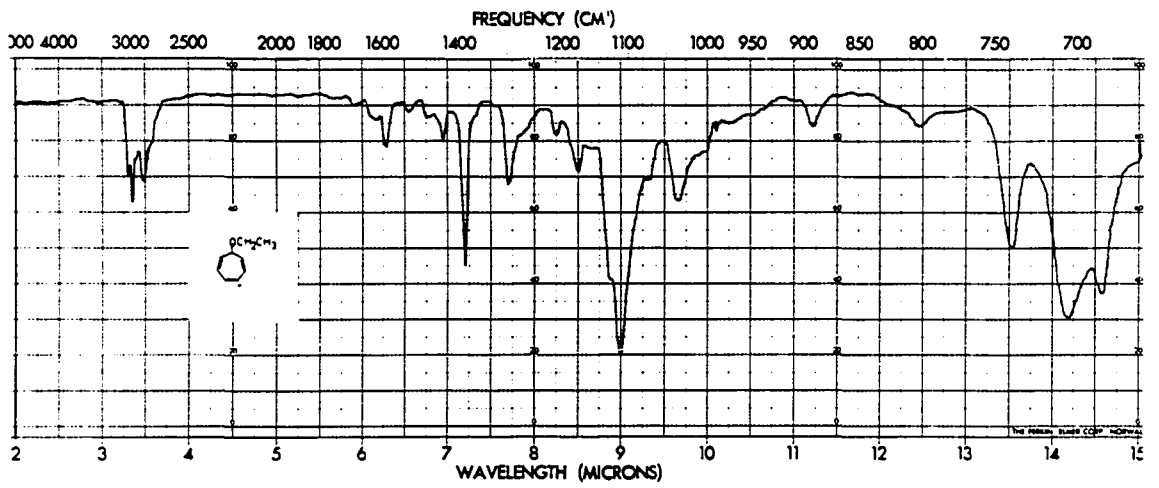
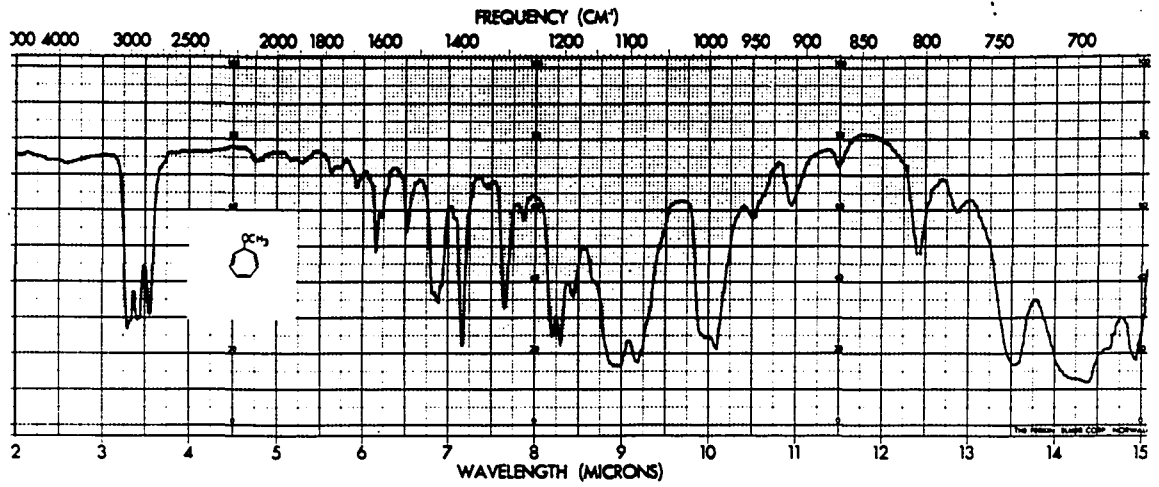


Figure 22. Infrared spectra

top: 1-Ethoxy-1,3,5-cycloheptatriene (LXXVIb)

middle: 1-Methoxybicyclo [3.2.0] hepta-3,6-
diene (LXXIVa)

bottom: 1-Ethoxybicyclo [3.2.0] hepta-3,6-
diene (LXXIVb)

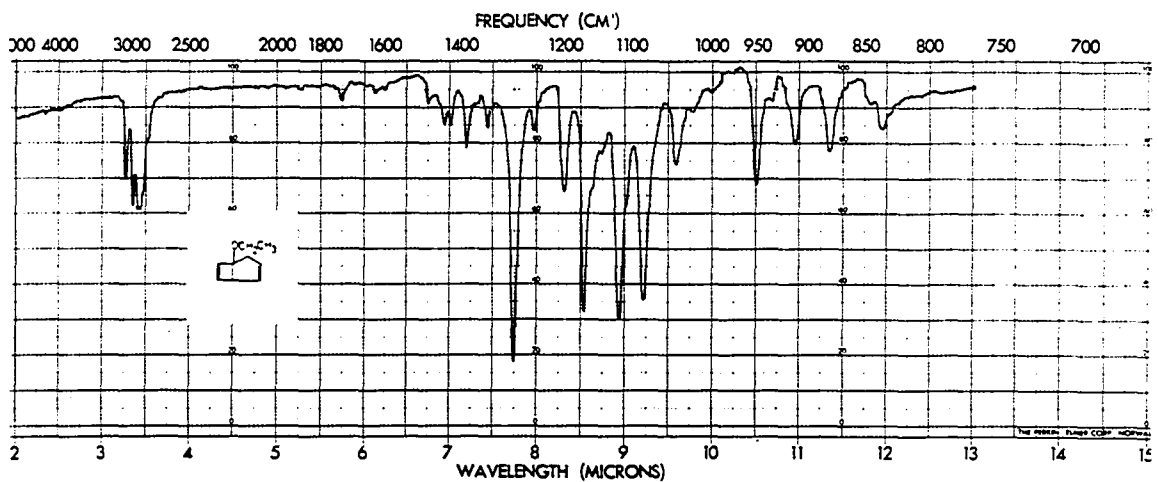
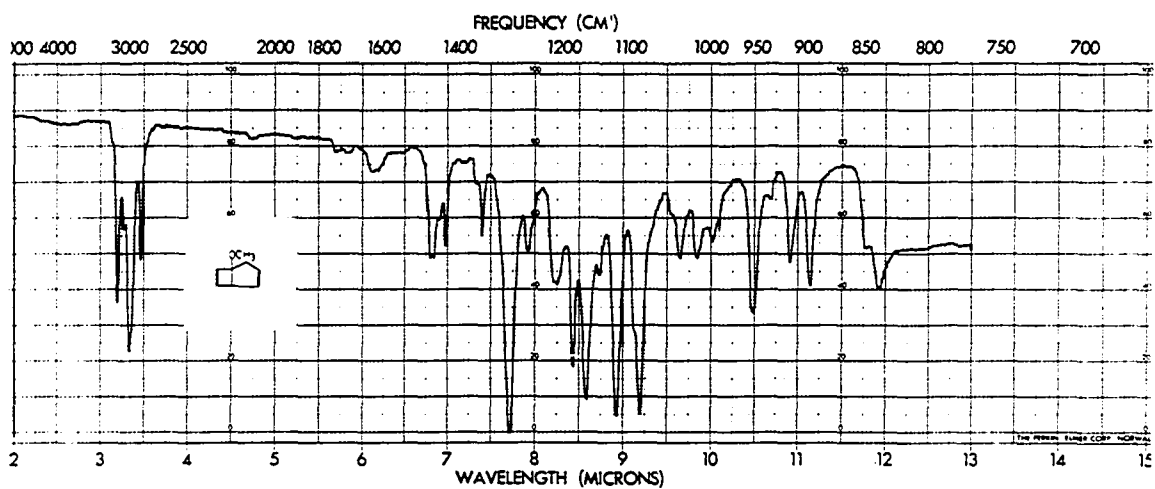
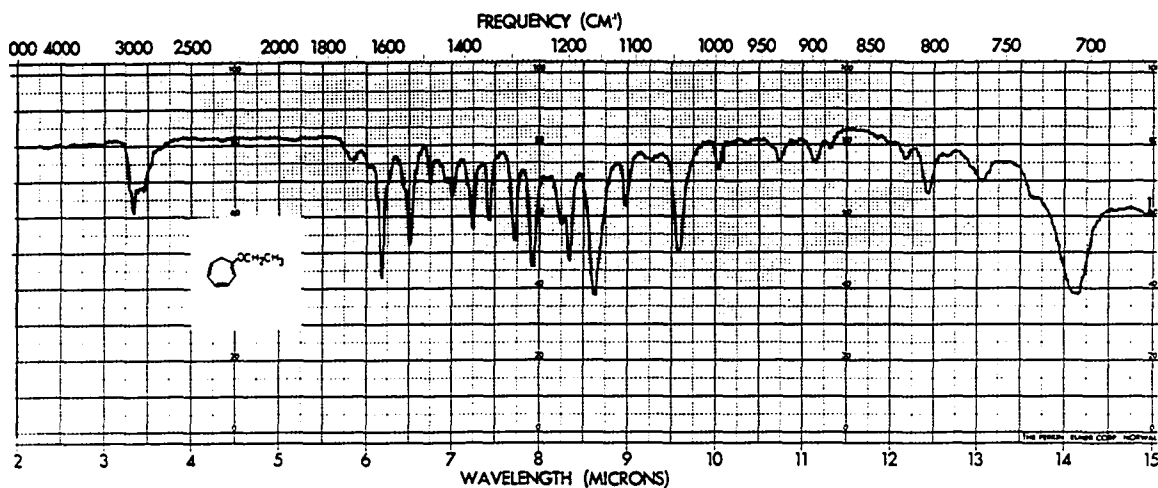


Figure 23. Infrared spectra

top: 1-Methoxybicyclo [3.2.0] heptane (LXXVa)

middle: 1-Ethoxybicyclo [3.2.0] heptane
(LXXVb)

bottom: 1-Methoxybicyclo [3.2.0] hept-3-ene
(LXXVIII)

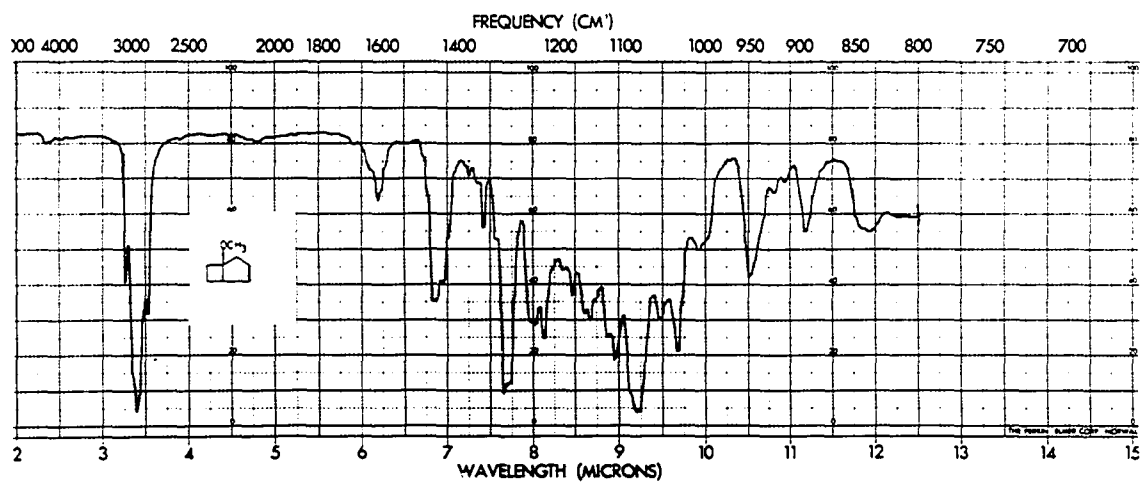
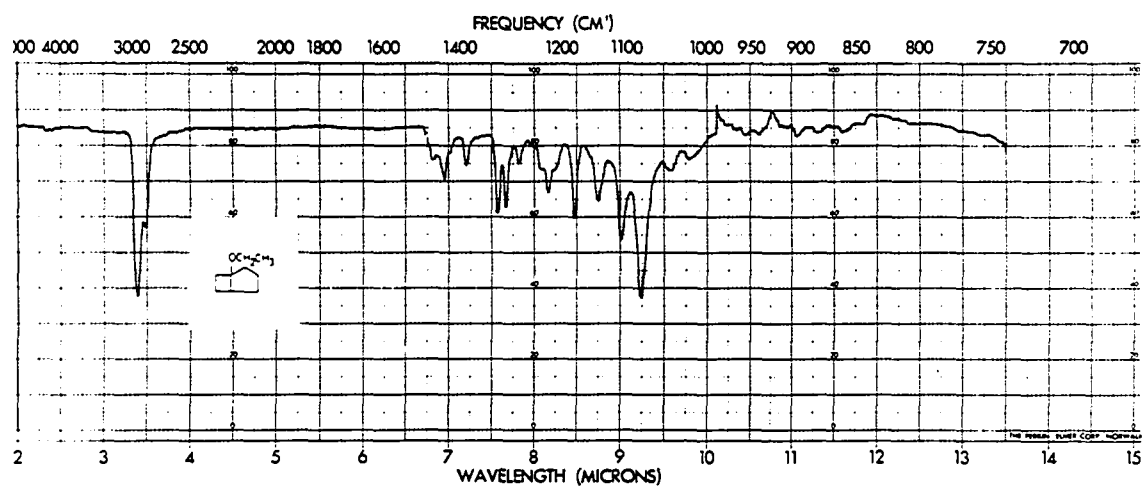
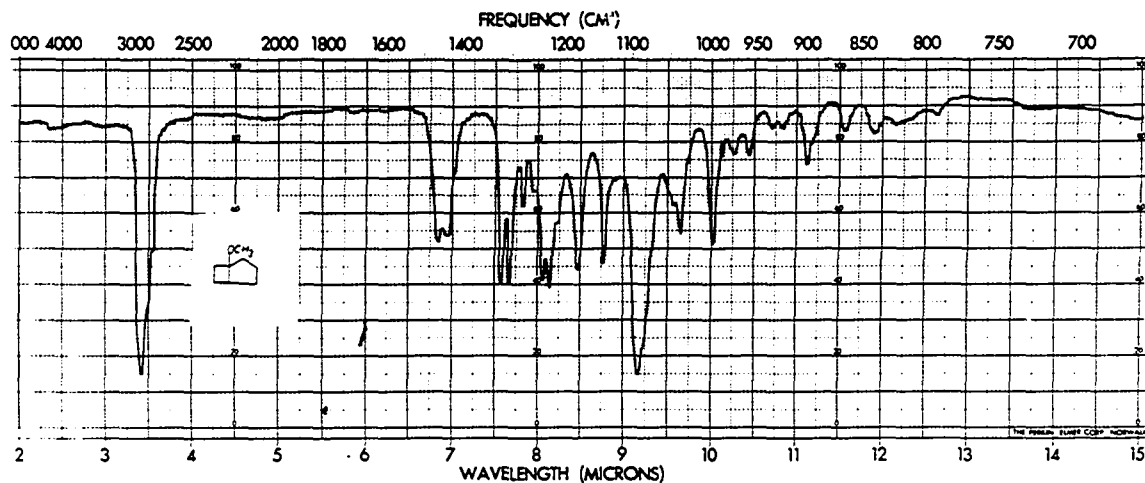


Figure 24. Nuclear magnetic resonance spectrum of tricyclo [5.1.0.0^{4,8}] oct-2-ene (XCII)

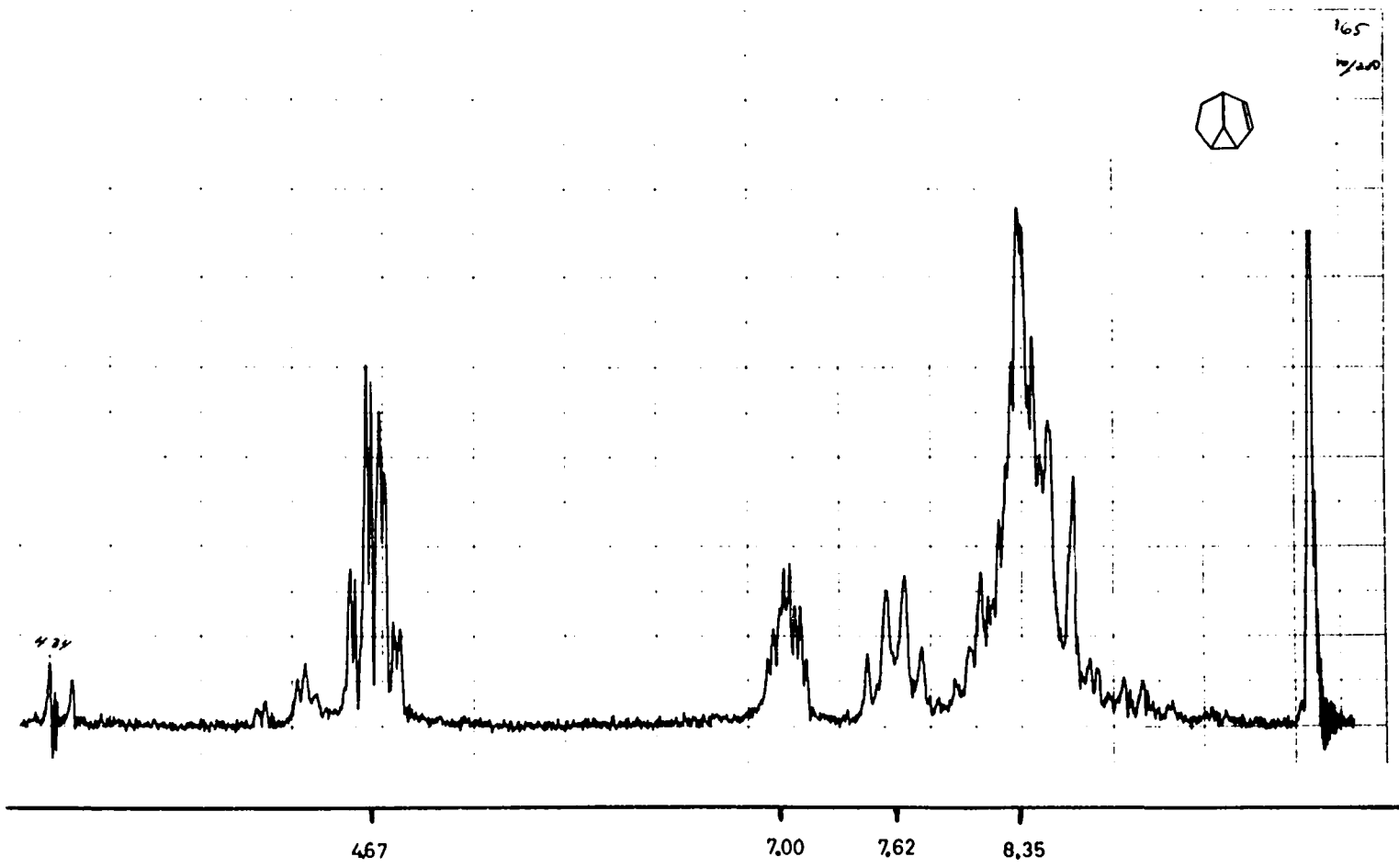


Figure 25. Nuclear magnetic spectra

top: 1-Methoxybicyclo [3.2.0] hept-3-ene
(LXXXIII)

bottom: Bicyclo [4.2.0] octa-2,7-diene (XCI)

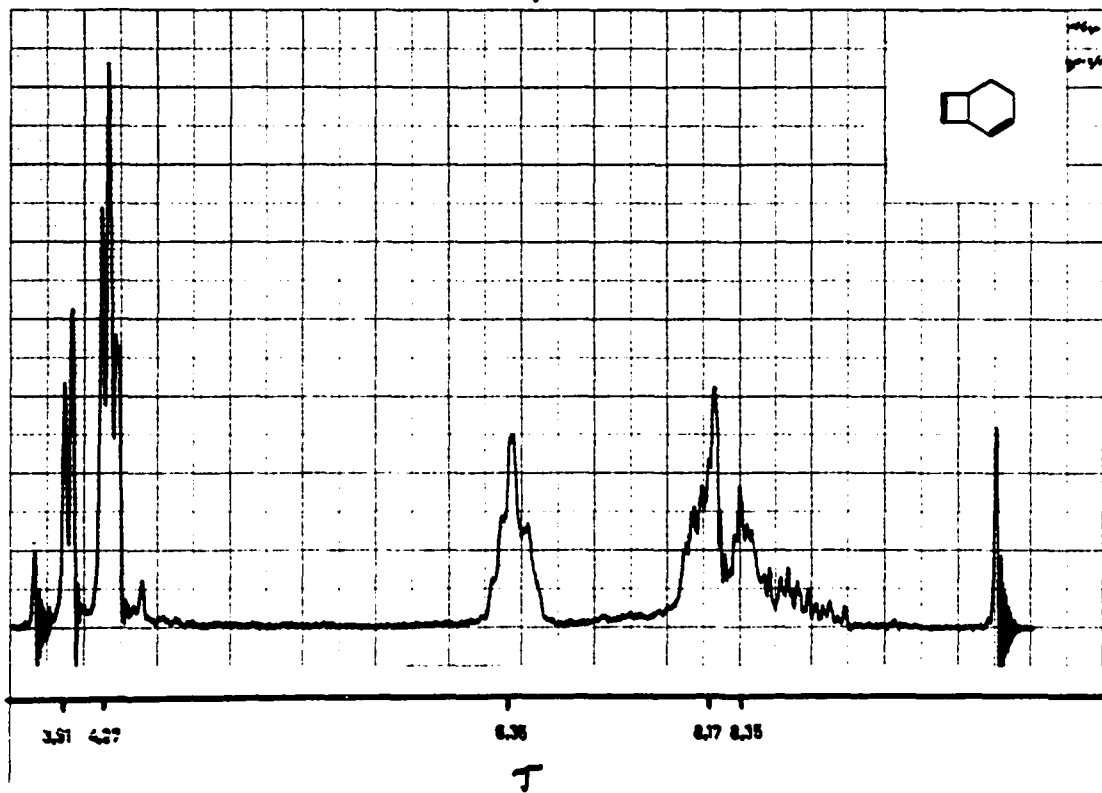
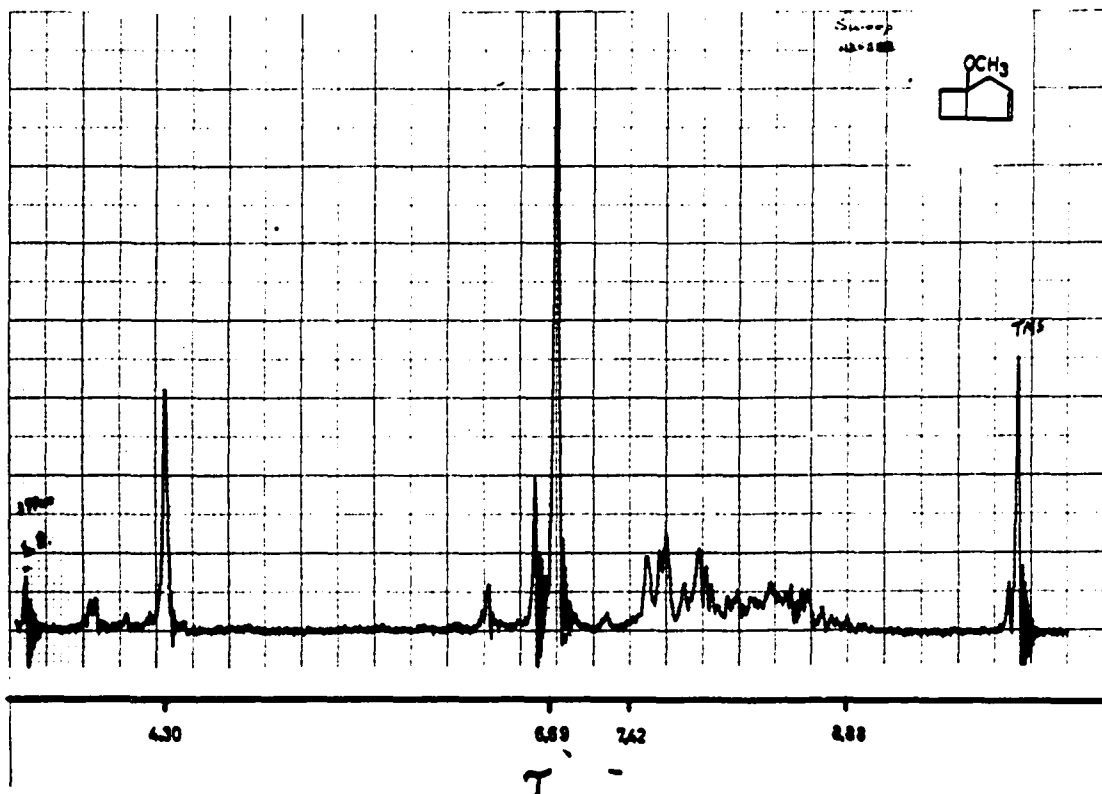
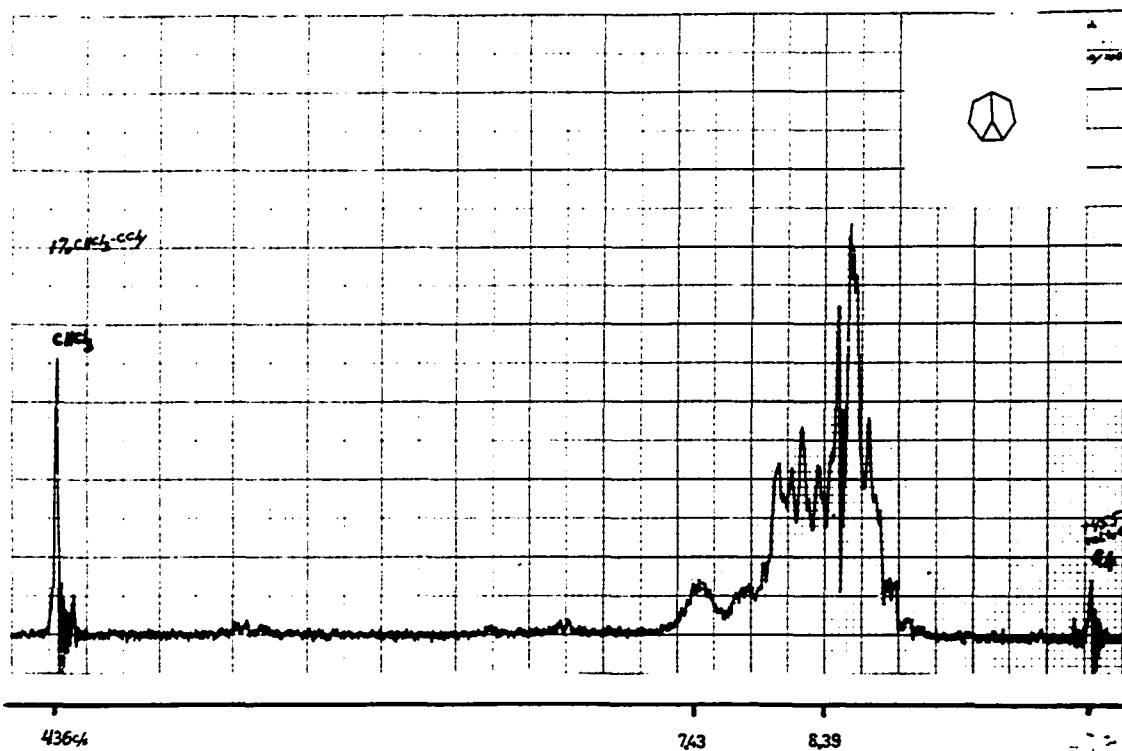


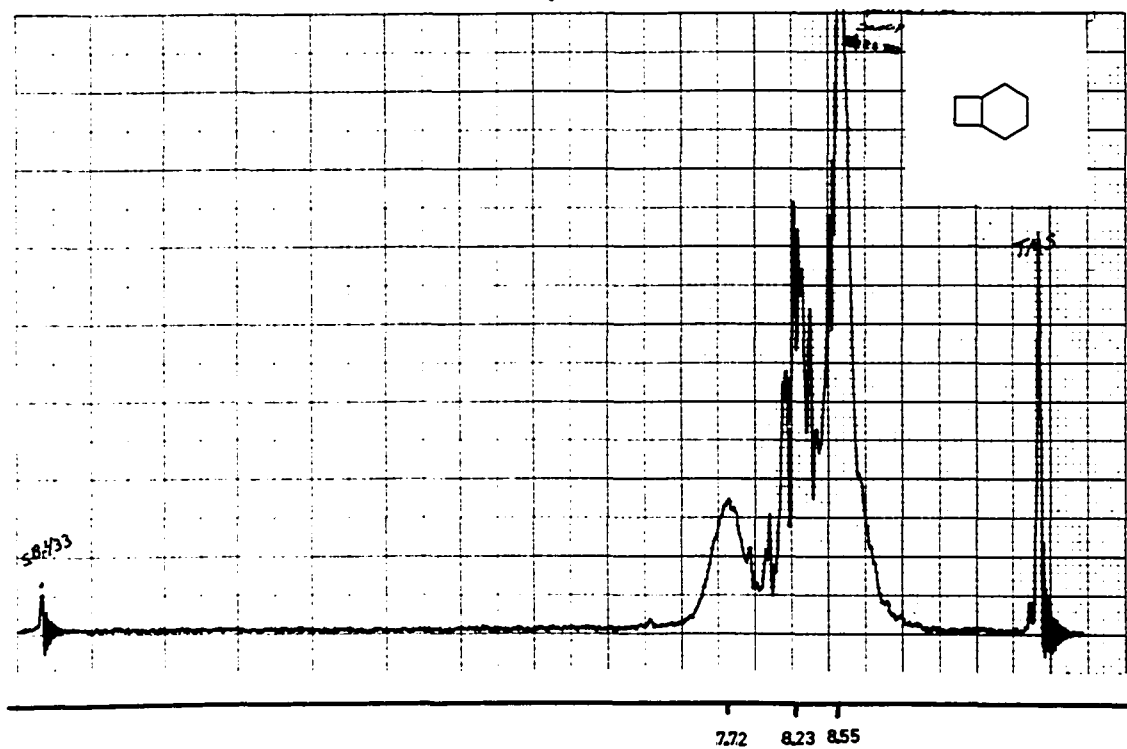
Figure 26. Nuclear magnetic resonance spectra

top: Tricyclo [5.1.0.0^{4,8}] octane (XCIV)

bottom: Bicyclo [4.2.0] octane (XCIII)



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Figure 27. Infrared spectra

top: Tricyclo [5.1.0.0^{4,8}] oct-2-ene (XCII)

bottom: Bicyclo [4.2.0] octa-2,7-diene (XCI)

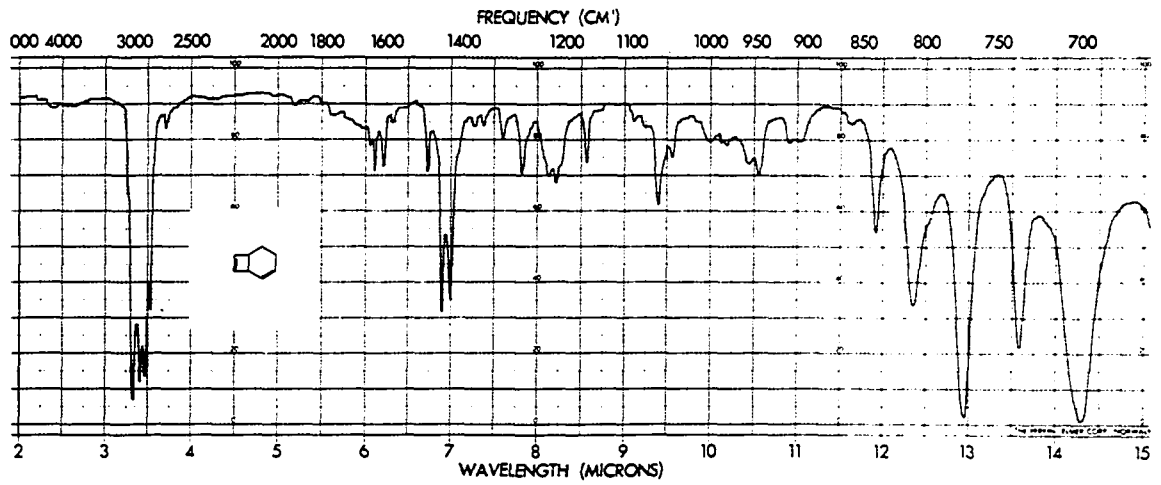
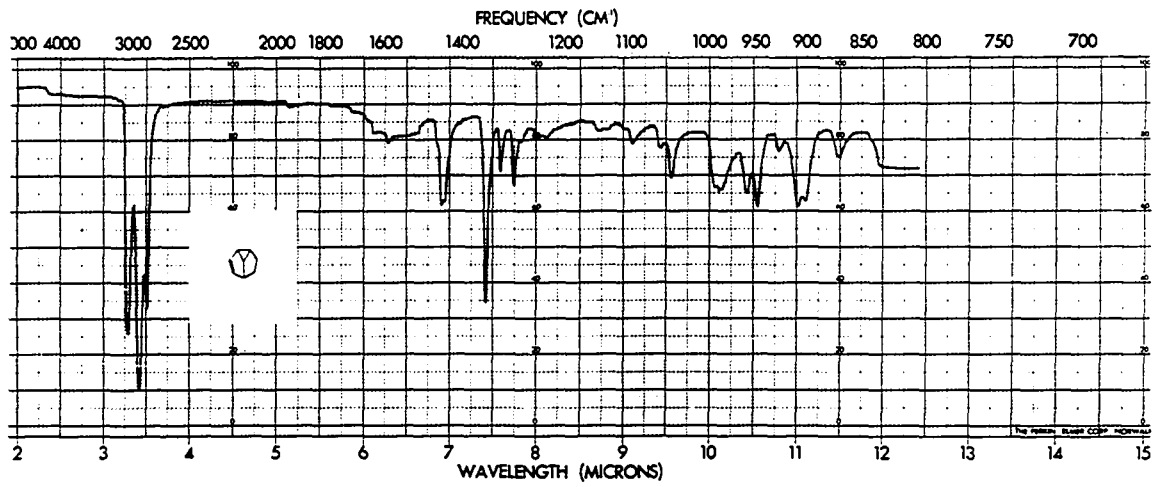
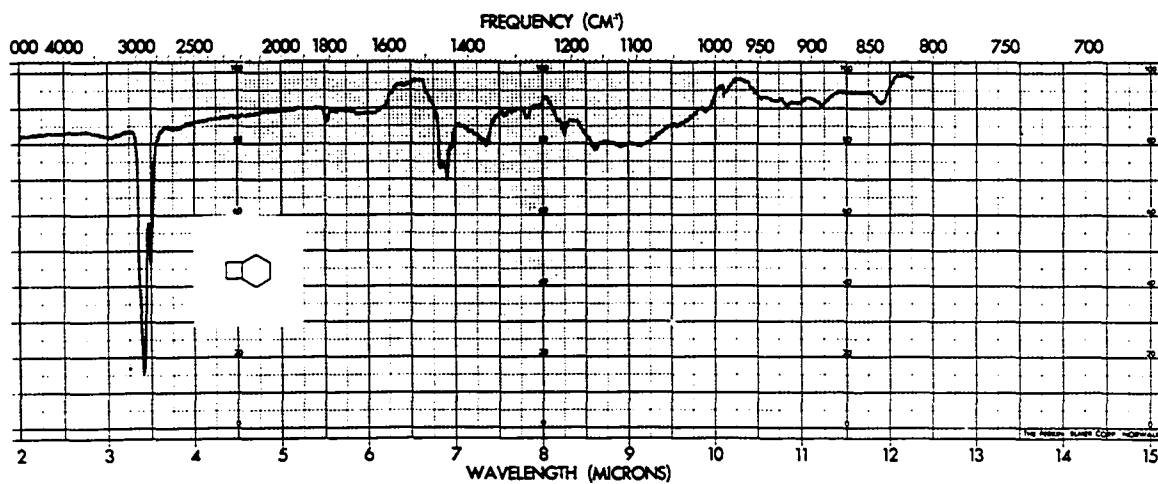
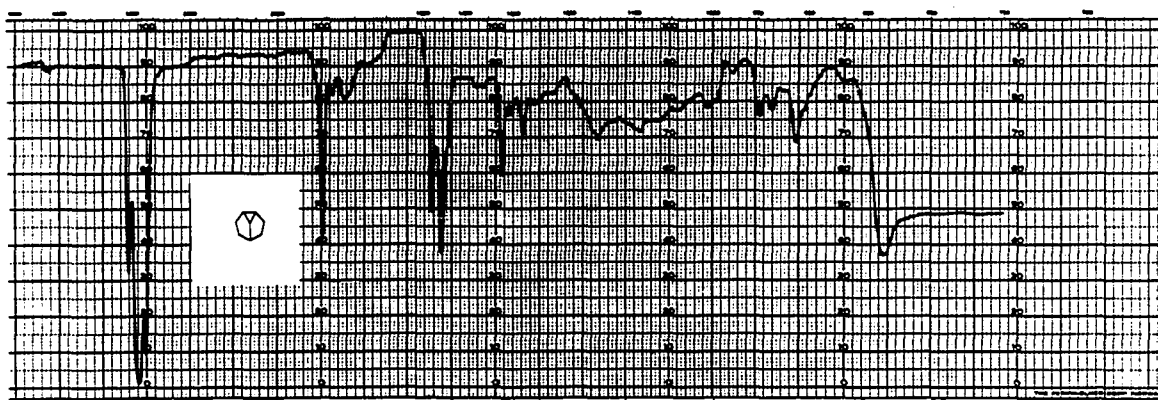


Figure 28. Infrared spectra

top: Tricyclo [5.1.0.0^{4,8}] octane (XCIV)

bottom: Bicyclo [4.2.0] octane (XCIII)



EXPERIMENTAL

Experimental for Photochemistry of 3,5-Cycloheptadienol and 2,4-Cycloheptadienol

Irradiation of 3,5 Cycloheptadienol (LXI) A solution of 1.7 g. of 3,5-cycloheptadienol (28) in one l. of anhydrous ether was irradiated 4 hours with a quartz jacketed Hammovia immersion lamp (type L). The ether was removed through a Vigreux column, giving 1.5 g. of crude photoproduct.

The crude photoproduct absorbed one equivalent of hydrogen over Adams catalyst in methanol. It was separated on a 3/8 in. by 6 ft. vapor phase chromatography column containing Ucon LB 550-X grease on 80-100 mesh Celite at 148° giving LXI (78%, retention time 11.8 min.) and LXII (22%, retention time 18.1 min.).

Anal. Calcd. for $C_7H_{10}O$: C. 76.32; H. 9.15. Found LXI: C. 76.20; H. 9.25; LXII: C. 76.20; H. 9.31.

Oxidation of endo-Bicyclo [3.2.0] hept-6-en-3-ol (LXI)
A solution of 8 N chromic acid in acetone (prepared according to the procedure of Bowers, Halsall, Jones, and Lemin) (46) was slowly added to a solution of endo-bicyclo [3.2.0] hept-6-en-3-ol (50 mg.) in 5 ml. of acetone at 0° until the solution maintained a persistent orange color. The solution was diluted with 25 ml. of water and extracted five times with ether (10 ml.). After drying over sodium sulfate, removal of the ether gave bicyclo [3.2.0] hept-6-en-3-one (c=o, 5.73u).

A sample of the product was purified for analysis by preparative scale vapor phase chromatography.

Anal. Calcd. for $C_7H_{10}O$: C. 77.75; H. 7.46. Found: C. 77.63; H. 7.58.

Oxidation of exo-Bicyclo [3.2.0] hept-6-en-3-ol (LXII)

Oxidation of exo-bicyclo [3.2.0] hept-6-en-3-ol as above gave bicyclo [3.2.0] hept-6-en-3-one identical in infrared absorption with the product obtained in the oxidation of endo-bicyclo [3.2.0] hept-6-en-3-ol.

Hydrogenation of Bicyclo [3.2.0] hept-6-en-3-one (LXIII)

Bicyclo [3.2.0] hept-6-en-3-one (70 mg.) in 15 ml. of methanol containing Adams catalyst absorbed one equivalent of hydrogen. Careful removal of the solvent gave bicyclo 3.2.0 heptan-3-one identical in infrared absorption to an authentic sample provided by Dr. R. Srinivasan (26). The semicarbazone of the product melted at 197-199° dec. pure and mixed with authentic bicyclo [3.2.0] heptan-3-one semicarbazone (26).

Lithium Aluminum Hydride Reduction of Bicyclo [3.2.0] hept-6-en-3-one (LXIII) A solution of bicyclo [3.2.0] hept-6-en-3-one (5 mg.) in 1 ml. of anhydrous ether was added to a slurry of lithium aluminum hydride (5 mg.) in 0.5 ml. of ether. The excess hydride was decomposed with moist sodium sulfate. Removal of the ether after drying over magnesium sulfate gave the mixed alcohols LXI and LXII. Vapor phase chromatographic analysis showed this to be a 9:1 mixture of LXI and LXII. The alcohols were identified by adding pure LXI and pure LXII

to separate samples of the mixture and observing the enhancement of the v.p.c. peaks due to each component.

Bicyclo [3.2.0] hept-6-en-2-ol (LXVII) A mixture of 2,4-cycloheptadienol and 3,5-cycloheptadienol (1.7 g.) obtained by lithium aluminum hydride reduction of the 2,4-cycloheptadienone-3,5-cycloheptadienone mixture obtained in the Hofmann degradation of tropinone methiodide (31), was dissolved in 100 ml. of anhydrous ether and irradiated in a quartz vessel with a General Electric UA-3 mercury arc lamp for 4 days. The solvent was removed under reduced pressure giving 1.5 g. of crude photoalcohols LXI, LXII, AND LXVII. This mixture was resolved by vapor phase chromatography on a 6 ft. by 3/8 in. column containing 15% Ucon LB 550-X on 80-100 mesh Celite at 148° into three alcohols with retention times 12.8 min. (LXI), 16.3 min. (LXVII) and 18.1 min. (LXII). The alcohols LXI and LXII were identified by comparison of infrared absorption and vapor phase chromatographic retention. The remaining alcohol (LXVII) showed nuclear magnetic resonance absorption at 4.08, 6.04, 6.70, 7.00, 7.96, and 8.27 μ .

Anal. Calcd. for C₇H₁₀O: C. 76.32; H. 9.15. Found: C. 76.18; H. 9.04.

Photochemistry of 3,5-Cycloheptadienone
and 2-Methyl-3,5-Cycloheptadienone

Irradiation of 2-Methyl-3,5-cycloheptadienone (LXVIII)

A solution of 2-methyl-3,5-cycloheptadienone (28) (0.73 g.)

in 100 ml. of ether in a quartz vessel equipped with an internal cooling coil and an outlet for gas collection was irradiated with a General Electric UA-3 mercury arc lamp for 6.5 hours. Carbon monoxide (95% of theory) was collected and identified by infrared comparison. The ethereal solution was concentrated by careful distillation, and the product was separated by preparative scale vapor phase chromatography. The product thus obtained showed $\left(\begin{array}{l} \text{EtOH} \\ \text{MAX.} \end{array} \right)$ 252 μ (26,800), 261 μ (36,400), 271 μ (28,900) and infrared maxima at 3.23, 3.32, 3.43, 3.51, 5.56, 6.11, 6.16, 6.91, 6.98, 7.29, 10.42, 10.67 and 11.19 μ .

A portion of the product absorbed 3.07 equivalents of hydrogen over palladium-on-carbon in pentane. The hydrogenation product was identified as n-heptane by comparison of vapor phase chromatographic retention and infrared absorption with an authentic sample.

Irradiation of 3,5-Cycloheptadienone (LXX) A solution of 3,5-cycloheptadienone (28) (2.73 g.) in 50 ml. of anhydrous ether was irradiated (General Electric UA-3 mercury arc lamp) in a quartz vessel fitted with an internal cooling coil and a gas collection apparatus. After 27 hours no more gas was evolved, and the irradiation was stopped. The gas which had been collected was identified as carbon monoxide by comparison of infrared spectra. The ether and low boiling product were separated from starting material by distillation. The product was separated from the ether by preparative scale vapor

phase chromatography on a 6 ft. by 3/8 in. column containing 15% Ucon LB 550-X on 80-100 mesh Celite at 71°. The product showed ultraviolet absorption at 246, 256, and 266 m μ and infrared maxima at 3.22, 3.31, 4.30, 5.52, 6.15, 6.90, 7.00, 9.95, 10.15, 10.67, and 11.10 μ in good agreement with the values reported for a mixture of cis- and trans-1,3,5-hexatrienes (32).

Experimental for the Photochemistry of
7-Alkoxy-1,3,5-Cycloheptatriene and
1-Alkoxy-1,3,5-Cycloheptatriene

7-Ethoxy-1,3,5-cycloheptatriene (LXXIIIb) A solution of 37 g. of tropylium chloride in 200 ml. of absolute ethanol was slowly neutralized with anhydrous sodium bicarbonate. The slurry was filtered and the filtrate was concentrated to 50 ml. Water (200 ml.) was added, and the solution extracted five times with 50 ml. portions of pentane. After drying over anhydrous sodium sulfate distillation of the pentane extract through a short Vigreux column gave 32.2 g. (87%) of 7-ethoxy-1,3,5-cycloheptatriene, b.p. 41° at 0.7 mm; $\lambda_{\text{max.}}^{\text{EtOH}}$ 257 log ϵ 3.57.

Anal. Calcd. C. 79.37; H. 8.88. Found: C. 79.17; H. 9.05.

7-Methoxy-1,3,5-cycloheptatriene (LXXIIIa) A stirred solution of 42 g. of tropylium chloride in 250 ml. of absolute methanol was slowly neutralized with sodium hydroxide pellets. After the addition of 500 ml. of water the solution was extracted six times with 50 ml. portions of pentane. Distillation

of the pentane extract after drying over anhydrous sodium sulfate gave 38.2 g. (91%) of 7-methoxy-1,3,5-cycloheptatriene, (47) b.p. 51° at 20 mm; λ_{max}^{EtOH} 256mu log 3.58.

Anal. Calcd. C. 78.65; H. 8.25. Found: C. 78.62; H. 8.26.

Irradiation of 7-Ethoxy-1,3,5-cycloheptatriene (LXXIIIb)

A solution of 10 g. of 7-ethoxy-1,3,5-cycloheptatriene in 2 l. of absolute ether was irradiated 8 hours with a quartz jacketed Hannovia immersion lamp (type A). Distillation of the ethereal solution through a short Vigreux column gave 9.1 g. (91%) of 1-ethoxybicyclo[3.2.0]hepta-3,6-diene, b.p. 47° at 21 mm.

Anal. Calcd. C. 79.37; H. 8.88. Found: C. 79.53; H. 8.83.

Irradiation of 7-Methoxy-1,3,5-cycloheptatriene (LXXIIIa)

A solution of 8 g. of methyl tropyli ether in 2 l. of absolute ether was irradiated 6 hours with a quartz jacketed Hannovia immersion lamp (type A). The solution was carefully concentrated to 50 ml. on a rotary evaporator. Distillation of the resulting concentrate through a short Vigreux column gave 7.4 g. (92%) of 1-methoxybicyclo[3.2.0]hepta-3,6-diene, b.p. 39° at 20 mm.

Anal. Calcd. C. 78.65; H. 8.25. Found: C. 78.83; H. 8.36.

Pyrolysis of 1-Ethoxybicyclo [3.2.0] hepta-3,6-diene (LXIVb) 2 g. of 1-ethoxybicyclo [3.2.0] hepta-3,6-diene

was dropped through a preheated (340°) vertical pyrolysis column packed with Pyrex helices in a stream of dry nitrogen. The exit end of the pyrolysis column was connected to a trap immersed in a Dry Ice-acetone bath. The product was identified as 1-ethoxy-1,3,5-cycloheptatriene by comparison of ultra violet, infrared and nuclear magnetic resonance spectra with that of an authentic sample (40).

Pyrolysis of 1-Methoxybicyclo [3.2.0] hepta-3,6-diene (LXXIVa) 2 g. of 1-methoxybicyclo [3.2.0] hepta-3,6-diene was pyrolyzed as above at 352° . The product was identified as 1-methoxy-1,3,5-cycloheptatriene by comparison of the NMR spectrum of the product with that of authentic 1-ethoxy-1,3,5-cycloheptatriene prepared by the procedure of Parham (37).

Pyrolysis of 7-Ethoxy-1,3,5-cycloheptatriene (LXXIIIb) Pyrolysis of 7-ethoxy-1,3,5-cycloheptatriene with the previously described apparatus maintained at 340° gave less than 30% conversion to 1-ethoxycycloheptatriene. Raising the column temperature to 410° gave complete conversion to 1-ethoxy-1,3,5-cycloheptatriene (yield 71%).

Pyrolysis of 7-Methoxy-1,3,5-cycloheptatriene (LXXIIIa) 7-methoxy-1,3,5-cycloheptatriene was pyrolyzed as described above. At 350° , the conversion was less than 40% complete. Upon raising to 420° the conversion to 1-methoxy-1,3,5-cycloheptatriene was complete. Yield 74%.

Irradiation of 1-Ethoxy-1,3,5-cycloheptatriene (LXXVIb) 1.2 g. of 1-ethoxy-1,3,5-cycloheptatriene in 1.5 l. of

anhydrous ether was irradiated 7 hours with a quartz jacketed Hannovia immersion lamp (type A). The solution was concentrated on a rotary evaporator, and distilled giving 1-ethoxybicyclo [3.2.0] hepta-3,6-diene (0.5 g., 42%) identified by comparison of nuclear magnetic resonance and infrared spectra with a sample prepared from the irradiation of 7-ethoxy-1,3,5-cycloheptatriene.

Irradiation of 1-Methoxy-1,3,5-cycloheptatriene (LXXVIa)

1.4 g. of 1-methoxy-1,3,5-cycloheptatriene in 2 l. of anhydrous ether was irradiated 9 hours with a quartz jacketed Hannovia immersion lamp (type A). The solution was concentrated on a rotary evaporator and distilled giving 1-methoxybicyclo [3.2.0] hepta-3,6-diene (0.6 g., 43%) identified by comparison of nuclear magnetic resonance and infrared spectra with that of a sample prepared by the irradiation of 7-methoxy-1,3,5-cycloheptatriene.

1-Ethoxybicyclo [3.2.0] heptane (LXXVb) A solution of 1-ethoxybicyclo [3.2.0] hepta-3,6-diene (73 mg.) in 3 ml. of carbon tetrachloride containing prereduced platinum oxide (20 mg.) absorbed 2.08 equivalents of hydrogen. The carbon tetrachloride solution was separated by preparative scale vapor phase chromatography on a 3/8 in. by 6 ft. Ucon LB 550X-chromsorb P(1:5) column. The product was collected in a Dry Ice-acetone cooled trap.

Anal. Calcd. C. 77.14; H. 11.43. Found: C. 76.86; H. 11.14.

1-Methoxybicyclo [3.2.0] heptane (LXXVa) A solution of 1-methoxybicyclo [3.2.0] hepta-3,6-diene (97 mg.) in 3 ml. of carbon tetrachloride containing prereduced platinum oxide (20 mg.) absorbed 2.05 equivalents of hydrogen. The solution was separated by vapor phase chromatography on a 3/8 in. by 6 ft. Ucon LB 550-X chromosorb P(1:5) column.

Anal. Calcd. C. 76.19; H. 11.11. Found: C. 76.02; H. 11.16.

1-Methoxybicyclo [3.2.0] hept-3-ene (LXXVIIIa) A solution of 1-methoxybicyclo [3.2.0] hepta-3,6-diene (2.74 g.) in 10 ml. of carbon tetrachloride containing 10% platinum on charcoal (50 mg.) was allowed to absorb one equivalent of hydrogen. Analysis by vapor phase chromatography showed one major product (95%). The nuclear magnetic resonance spectrum showed no cyclobutene protons, but did show cyclopentene protons, 4.30 τ .

Conversion of 1-Methoxybicyclo [3.2.0] hept-3-ene to 1.4-Cycloheptanedione (LXXX) A mixture of sodium borohydride (0.55 g.) and anhydrous zinc chloride (0.1 g.) (38) in 20 ml. of anhydrous ether was stirred for 1.5 hours under a nitrogen atmosphere. A solution of 1-methoxybicyclo [3.2.0] hept-3-ene (6.2 g.) in 15 ml. of anhydrous ether was added, and then 2.2 g. of boron trifluoride etherate in 5 ml. of anhydrous ether was added dropwise over a 1 hour period. After stirring for 2 hours, excess hydride was destroyed with 2 ml. of water. The dichromate, 4 ml. of concentrated sulfuric acid, and

diluted with water to 25 ml. was added to the stirred solution over a 15 minute period. After heating under reflux for 2 hours the upper layer was separated and the aqueous layer extracted twice with 10 ml. portions of ether. The ether solutions were combined, dried over anhydrous sodium sulfate, and carefully concentrated to 20 ml. Treatment of a 5 ml. portion of the ether concentrate with 2,4-dinitrophenylhydrazine in ethanolic acid (48) gave after recrystallization from nitrobenzene-ethanol mixture, orange crystals, m.p. 242-243° shown to be the bis-2,4-dinitrophenylhydrazone of cycloheptane-1,4-dione by mixed melting point and comparison of infrared spectra with an authentic sample (20,39). To a 5 ml. portion of above ether concentrate was added 1 g. of n-butyl-ether. Analysis of this mixture by vapor phase chromatography showed only ether, n-butyl ether, and cycloheptane-1,4-dione as volatile components. Yield of cycloheptane-1,4-dione based on starting 1-methoxybicyclo[3.2.0]hept-3-ene was 21%. Attempts to isolate any other ketones formed in the hydroboration-oxidation (38) reaction were unsuccessful.

Benzophenone-sensitized Irradiation of 7-Ethoxy-1,3,5-cycloheptatriene (LXXIIIb) 1 g. of 7-ethoxy-1,3,5-cycloheptatriene in 400 ml. of anhydrous ether was irradiated 5 hours with a Pyrex jacketed Hannover immersion lamp (type A). Comparison of the ultraviolet absorption before and after 5 hours of irradiation showed no change in the solution.

Benzophenone (13.4 g.) (33) was added to the above solution and the irradiation continued for 5 hours. The solution was concentrated on a rotary evaporator and analyzed by vapor phase chromatography (49) on a 3/8 in. by 6 ft. Ucon LB 550X-chromsorb P(1:5) column. This showed a 21% conversion to 1-ethoxybicyclo [3.2.0] hepta-3,6-diene.

Vapor Phase Irradiation of 7-Methoxy-1,3,5-cycloheptatriene (LXXIIIa) 1.2 g. of 7-methoxy-1,3,5-cycloheptatriene was irradiated in an apparatus consisting of two Dry Ice-acetone cooled traps connected to each end of a 3 in. diameter by 4 in. high coil of 10 mm. O. D. quartz tubing 12 ft. long. A type A Hannoveria immersion lamp was mounted in the center of the coil. The sample was placed in one cold trap and the system evacuated to .05 mm. of mercury. The Dry Ice-acetone trap was removed and the sample allowed to diffuse through the coil to the other cold trap. The process was repeated three times. Vapor phase chromatography analysis of the product showed 14% unreacted starting material, 38% 1-methoxy-1,3,5-cycloheptatriene, and 48% 1-methoxybicyclo-[3.2.0] hepta-3,6-diene.

Experimental for the Photochemistry of
1,3,5-Cyclooctatriene

1,3,5-Cyclooctatriene (LXXXIX) 3-bromo-1,5-cyclooctadiene (prepared by the method of Cope, Stevens, and Hochstein) (50) was dehydrobrominated by a modification of

the procedure of Inhoffen, Kranse, and Bork (54). 3-bromo-1,5-cyclooctadiene (120 g.) was refluxed for 2 hours with collidine (100 g.) under a nitrogen atmosphere. The liquid was separated, and the solid was washed twice with 100 ml. portions of ether. The combined ether solution was washed twice with 100 ml. of 0.1 N sulfuric acid, twice with dilute sodium bicarbonate, and twice with water. After drying over anhydrous sodium sulfate the ether solution was distilled through a short Vigreux column giving 1,3,5-cyclooctatriene (29 g., 42%).

Irradiation of 1,3,5-Cyclooctatriene (LXXXIX) A

solution of 25 g. of 1,3,5-cyclooctatriene in 2 l. of absolute ether was irradiated for 220 hours with a quartz jacketed Hannovia immersion lamp (type A). The ether solution was carefully concentrated to 50 ml. using a rotary evaporator. The products were separated by vapor phase chromatography using a 3/8 in. by 12 ft. copper column filled with 5% Ucon LB 550-X on 60-80 mesh chromsorb P. The total yield of volatile components was 41%. Three major compounds were isolated as follows: XCI 38%, retention time 10 minutes, XCII 14%, retention time 11.9 minutes, and 1-5cyclooctadiene (48%) identified by comparison with an authentic sample, (shoulder) λ^{EtOH} 208 μ (5300).

Anal. Calcd. for C₈H₁₀O: C. 90.51; H. 9.49. Found: XCI C. 90.39; H. 9.75. Found: XCII C. 90.50; H. 9.56.

Mol. wt. determination XCII calcd. 106. Found 111.*

Hydrogenation of Bicyclo [4.2.0] octa-2,7-diene (XCI)

A solution of bicyclo [4.2.0] octa-2,7-diene (271 mg.) in 3 ml. of carbon tetrachloride containing 10% platinum on charcoal (50 mg.) absorbed 1.96 equivalents of hydrogen. The product was shown to be bicyclo [4.2.0] octane by comparison of nuclear magnetic resonance and infrared spectra with a sample prepared by the hydrogenation of bicyclo [4.2.0] oct-7-ene (25,41).

Bicyclo [4.2.0] octane (XCIII)

A solution of bicyclo [4.2.0]-oct-7-ene (47 mg.) (25,41) in 5 ml. of carbon tetrachloride containing 10% platinum on charcoal (50 mg.) absorbed 1.02 equivalents of hydrogen. The solution was filtered and used directly for spectral comparison with a sample prepared from the hydrogenation of bicyclo [4.2.0] octa-2,7-diene.

Tricyclo [5.1.0.0^{4,8}] octane (XCIV)

A solution of tricyclo [5.1.0.0^{4,8}] oct-2-ene (211 mg.) in 3 ml. of carbon tetrachloride containing 10% platinum on charcoal (50 mg.)

*Molecular weights were determined using a Vapor Pressure Osmometer, Model 301A, Mechrolab Inc., Mountain View, California. The reference compound was 1,3-cyclooctadiene, and the solvent was carbon tetrachloride or 1% chloroform in carbon tetrachloride.

absorbed 0.99 equivalents of hydrogen. This solution was filtered and used directly for nuclear magnetic resonance and infrared analysis. Mol. wt. determination (XCIV)
Calcd. 108; Found: 111.

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APPENDIX

Vapor phase chromatography columns used in this investigation.

- 2 meter Perkin-Elmer: 2 meter by $\frac{1}{4}$ in. stainless steel tube packed with 20% by weight UCON-LB550X (poly alkyl ethers manufactured by Union Carbide Corporation) on a diatomaceous earth support; maximum temperature 200°.
- 6 ft. preparative scale UCON-LB550X: 6 ft. by $\frac{3}{8}$ in. copper tube packed with UCON-LB550X (15% by weight) on 80-100 mesh Celite (a white diatomaceous earth manufactured by Johns-Manville Corporation) or 60-80 mesh Chromsorb P (a pink diatomaceous earth distributed by F & M Corporation); maximum temperature 200°.
- 12 ft. preparative scale UCON-LB550X: 12 ft. by $\frac{3}{8}$ in. copper tube packed with UCON-LB550X (5% by weight) on 60-80 mesh Chromsorb P; maximum temperature 200°.