THE SILVER CATION ASSISTED REARRANGEMENT OF π-BROMOTRICYCLENE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
JANICE ELAINE KAROGLAN
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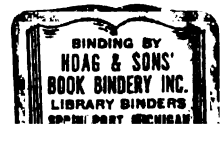
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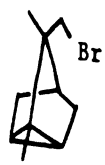

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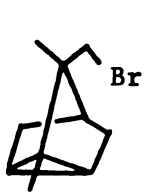
ABSTRACT

THE SILVER CATION ASSISTED REARRANGEMENT OF π-BROMOTRICYCLENE

by Janice Elaine Karoglan

The camphor derivative, π-bromotricyclene (I), was subjected to reaction with wet silver perchlorate in acetone which yielded the olefin II as the major product. This result was contrasted with the similar reaction of 3-nortricyclylcarbinyl bromide (III) to produce the alcohols IV and V.



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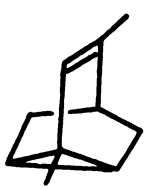

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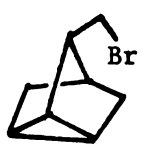

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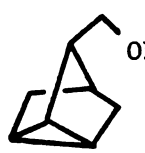

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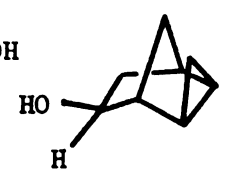

V

The structure of 2,4-dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene (II) was determined by spectroscopic evidence and by conversion of the olefin to the corresponding alcohol and ketone.

By comparing the silver cation assisted rearrangements of I and III, the effects of the methyl groups in I on cyclopropane participation could be determined. As a result, two mechanistic paths were formulated for this reaction.

THE SILVER CATION ASSISTED REARRANGEMENT OF π-BROMOTRICYCLENE

By

Janice Elaine Karoglan

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1969

To the memory of my father

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ACKNOWLEDGMENTS

The author wishes to express her sincere appreciation to Professor William H. Reusch for his guidance and encouragement during the course of this investigation, as well as for his patience with both the research and the researcher.

Special thanks are extended to Professor R. R. Sauers of Rutgers University for providing copies of infrared and nmr spectra; to Professor M. W. Rathke for his assistance with and discussions concerning hydroboration techniques; to Mr. Roger Wheaton for aid in preparation of the thesis figures; to many friends and associates; to my mother for her support and understanding throughout my years of study; and, lastly, to K.L.T. for an unending supply of ice cream cones.

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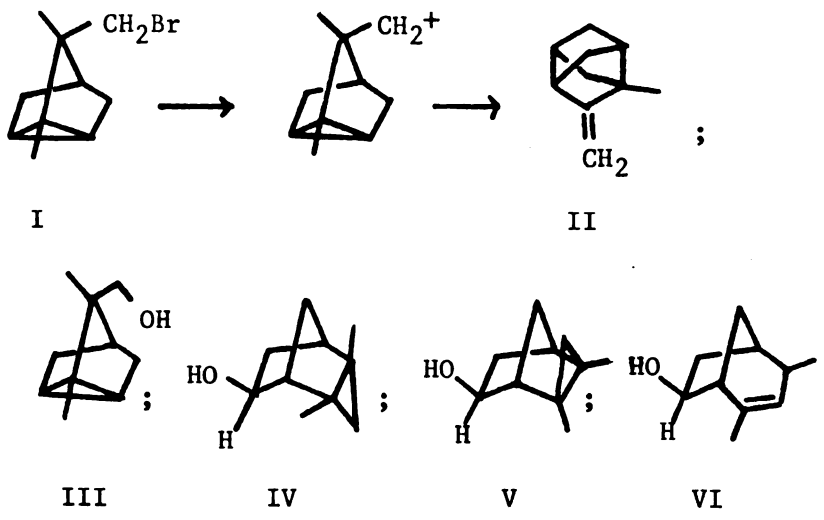
INTRODUCTION

"In a scientific pursuit there is continual food for discovery and wonder."

-- Frankenstein (M. Shelley)

Investigations into the chemistry of camphor and its derivatives date back to the 16th century and have been the concern of such pre-eminent workers as the alchemist Libavius (1595), Boyle (1667), Lavoisier, Berthelot (1859), Meyer (1870), Dumas (1883), Bredt (1893), Tiemann (1895), Perkin (1898);[1,2] and, more recently, Woodward (1941) and Corey (1957).[3] As a starting material, camphor has been the synthetic progenitor of a number of natural products as well as of systems for subsequent solvolytic and kinetic studies.

In this study the camphor derivative, π-bromotricyclene (I), was subjected to reaction with wet silver perchlorate in acetone. It was thought that participation of the cyclopropane ring in the ionization step could lead to the formation of the tricyclic olefin II or one or more of the alcohols III - VI, related to the solvolysis products from the 3-nortricyclylcarbinyl systems (Figure 1).[4]



I II III IV V VI

Figure 1. Expected Solvolysis Products of π-Bromotricyclene

In a comparative study, 3-nortricyclylcarbinyl bromide, which differs from the tricyclene derivative only in the absence of two methyl groups, was allowed to undergo a similar silver ion assisted solvolysis. From this reaction, the extent and importance of the effect of the methyl groups in the tricyclene system on cyclopropane participation could be determined. Also, the results of the solvolysis of 3-nortricyclylcarbinyl bromide in acetic acid as solvent were compared to those obtained by R. R. Sauers and workers as cited above.

Cyclopropane participation has been studied in cyclopropyl carbinyl systems by Sargent, Taylor, and Demisch[5] and for tricyclo[3.2.1.$0^{2,7}$]oct-4-yl functions by J. A. Berson and collaborators.[6] The work of Parker, Eakin, and Martin[7] has focused attention on transannular cyclopropyl participation in the bicyclo[3.3.1]nonane ring system. These studies, along with those reported by Tanida, Tsuji, and Irie on the solvolysis of endo-anti-tricyclo[3.2.1.$0^{2,4}$]-

octan-8-yl-p-nitrobenzoate[8] and by Battiste and associates on the possibility of non-classical cation formation in 7-norbornyl systems[9], show that cyclopropane participation is very dependent on, if not completely controlled by, the relative orientation of the three membered ring with the incipient cation. Furthermore, a relationship between ring strain and the degree of rearrangement likely to occur in a particular system has been suggested in the work of Sauers, Beisler, and Feilich cited above.

RESULTS AND DISCUSSION

The synthesis of π-bromotricyclene (I) from commercially available dl-camphor was accomplished as shown in Figure 2.

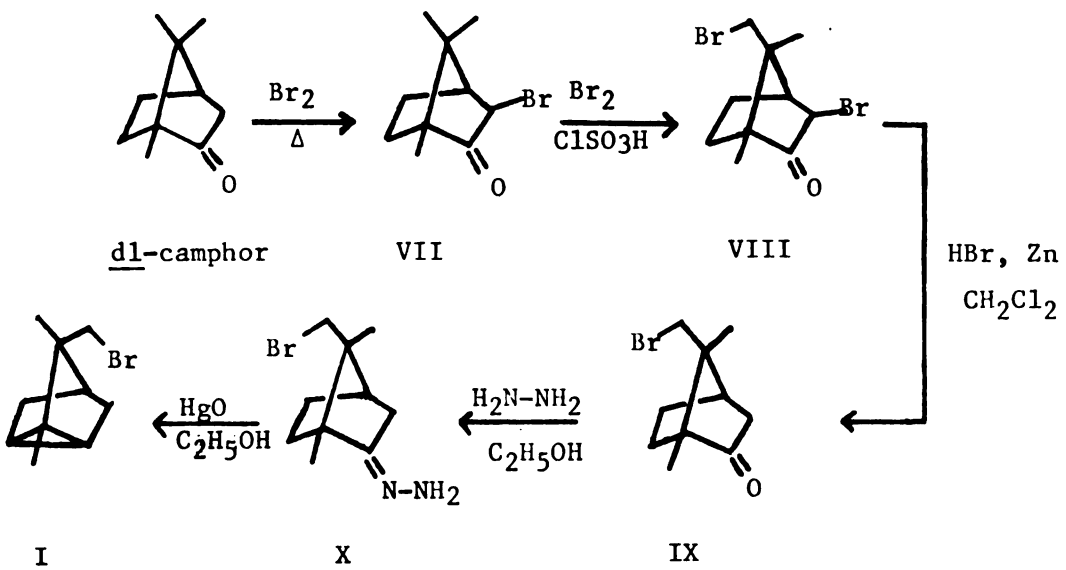


Figure 2. Synthesis of π-Bromotricyclene (I)

α-Bromocamphor (VII) was easily prepared by the procedure outlined by Kipping and Pope.[10] The subsequent conversion of VII to α,π-dibromocamphor (VIII), π-bromocamphor (IX), and π-bromocamphor hydrazone (X) followed the procedures of E. J. Corey and coworkers in the syntheses of α-santalene and trans-$\Delta^{11,12}$-iso-α-san-

talene.[11] Oxidation of X by mercuric oxide in ethanol yielded the tricyclic product I in 69% yield. A mechanism incorporating a carbene intermediate was proposed for this reaction by Meerwein in 1920 and confirmed by Reusch and colleagues in 1960 (Figure 3).[12,13]

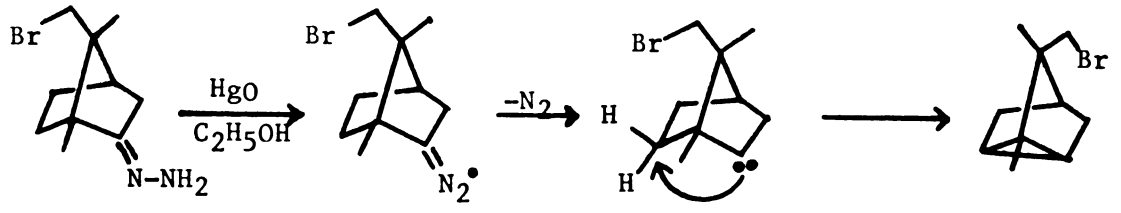
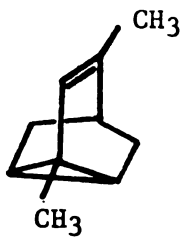


Figure 3. Mechanism of Mercuric Oxide Oxidation of π-Bromocamphor Hydrazone (X)

The action of wet silver perchlorate on a solution of I in acetone was found to yield three products after the crude reaction mixture was clarified by passage through a silica gel column. The components of the resulting solution proved to be difficult to separate by distillation; therefore, isolation and purification were finally accomplished by use of vapor phase chromatography (SE-30 column, 3/8" x 20'). The component of shortest retention time was shown to be diacetone alcohol by comparison (infrared spectrum and vpc retention time) with an authentic sample. A second component of intermediate retention time (15 minutes) was formed in 41.8% yield, and has been assigned the structure XI. This compound was a highly volatile, pale yellow liquid with a camphor-like odor. The third minor component was not studied.



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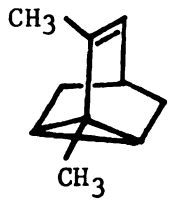

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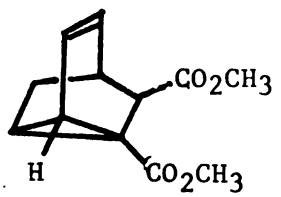


XII

The structure elucidation of the hitherto unknown 2,4-dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene (XI) was a lengthy, but nonetheless interesting task; for two structures, XI and XI', proved to be consistent with the spectroscopic evidence. Cyclopropyl hydrogens were shown to be present by infrared absorptions at 3050-3025 cm^{-1} (s), 1015 cm^{-1} (w), and 830 cm^{-1} (s) (Figure 4). Overtones of the 3025 cm^{-1} band were observed in the near infrared in the regions of 5900 cm^{-1} and 7300 cm^{-1}. The presence of an olefinic bond was disclosed by absorptions at 975 cm^{-1} and 1650 cm^{-1}, and confirmed by testing with tetranitromethane which afforded a rusty-orange colored spot. However, hydrogenation of XI over palladium on charcoal in ethyl acetate gave inconsistent results, indicating incomplete reduction of the olefinic linkage as evidenced by weakening of the 975 cm^{-1} infrared absorption and/or partial hydrogenolysis of the cyclopropyl ring bonds. These observations are in accord with recent studies of Poulter and Heathcock, which demonstrate that catalytic reduction of conjugated cyclopropyl alkenes is indeed often accompanied by hydrogenolysis of allylic cyclopropyl ring bonds. These workers also found that reduction

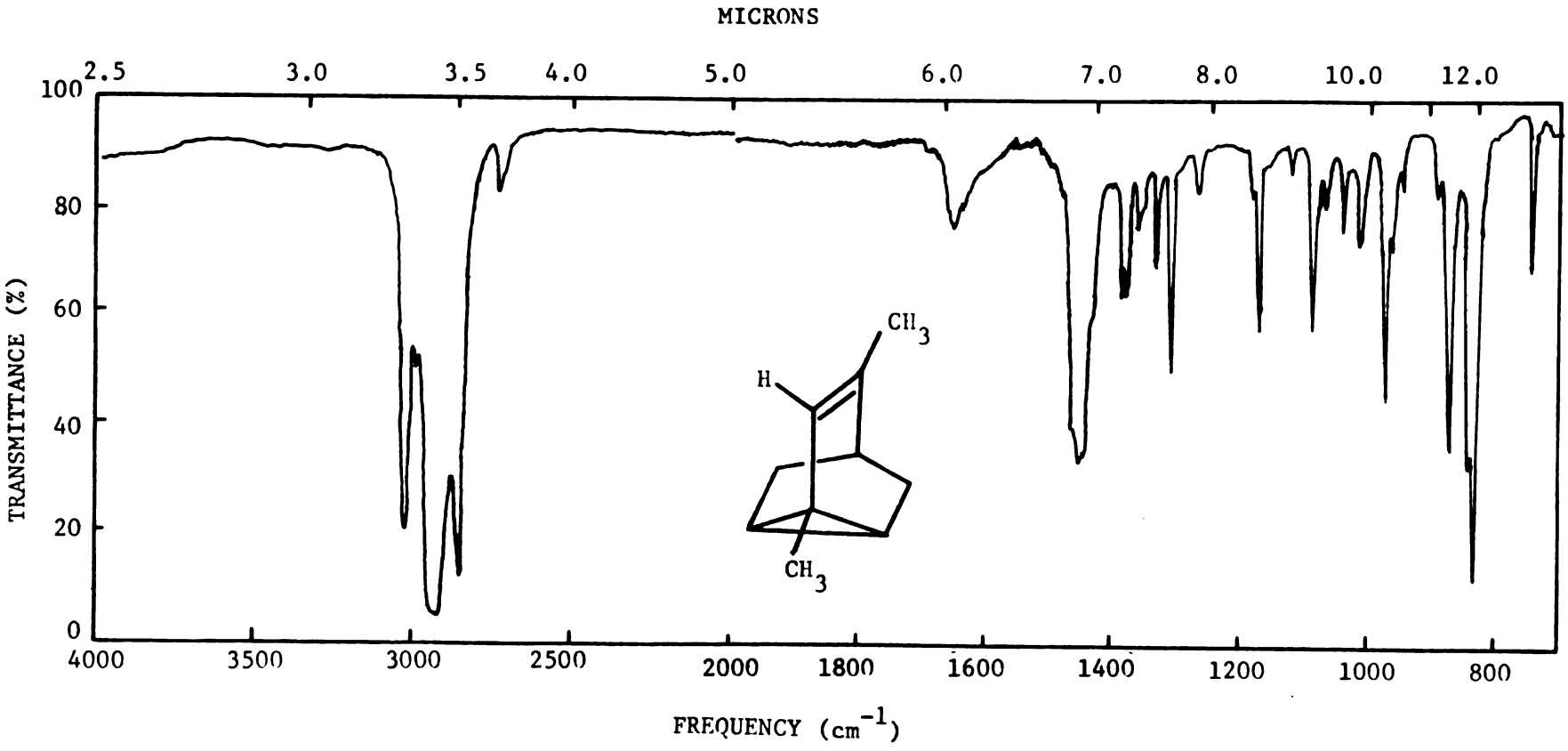


Figure 4. Infrared Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene (XI)

over palladium gave a greater degree of ring hydrogenolysis than did reduction over other common catalysts.[14,15]

The mass spectrum of XI revealed a molecular weight of 134 with %(P+1) = 11.2 and %(P+2) = 0.8 (theoretical P+1 = 11.03%, P+2 = 0.6%). Fragmentation patterns were not very informative. Ultraviolet absorption in cyclohexane gave λ_{max} = 206 mμ (log ε = 3.74). This is comparable to the value obtained by Huebner et al. for compound XII, $\lambda_{max}^{ethanol}$ = 208 mμ (log ε = 3.73), and strongly suggests a cyclopropane ring in conjugation with a double bond.[16]

By far the most lucid piece of information was the nmr spectrum shown in Figure 5. The high field three proton singlet (8.8 τ) indicates a quaternary methyl group, shifted slightly downfield by its attachment to the cyclopropane ring. The three proton doublet (8.3 τ, J = 2 cps) and the one proton multiplet (4.7 τ, J = 2 cps) show a methyl group and a vinylic hydrogen, H_a, oriented cis about the double bond and splitting one another. This assignment was confirmed by a double resonance experiment (Figure 6). The highest field signals (9.3, 9.1 τ; J = 11 cps) are attributed to H_b, which are strongly shielded by the olefinic bond. A multiplet in the region 8.4--8.7 τ is assigned to H_c, and the two proton singlet at 9.0 τ to H_d. The remaining signal at 7.7 τ is due, then, to H_e. These results and consequent structural assignment are consistent with the work of Vorozhtsov and collaborators[17] and closely agree with the data obtained by Huebner and coworkers on compound XII as outlined below (Figure 7).[16]

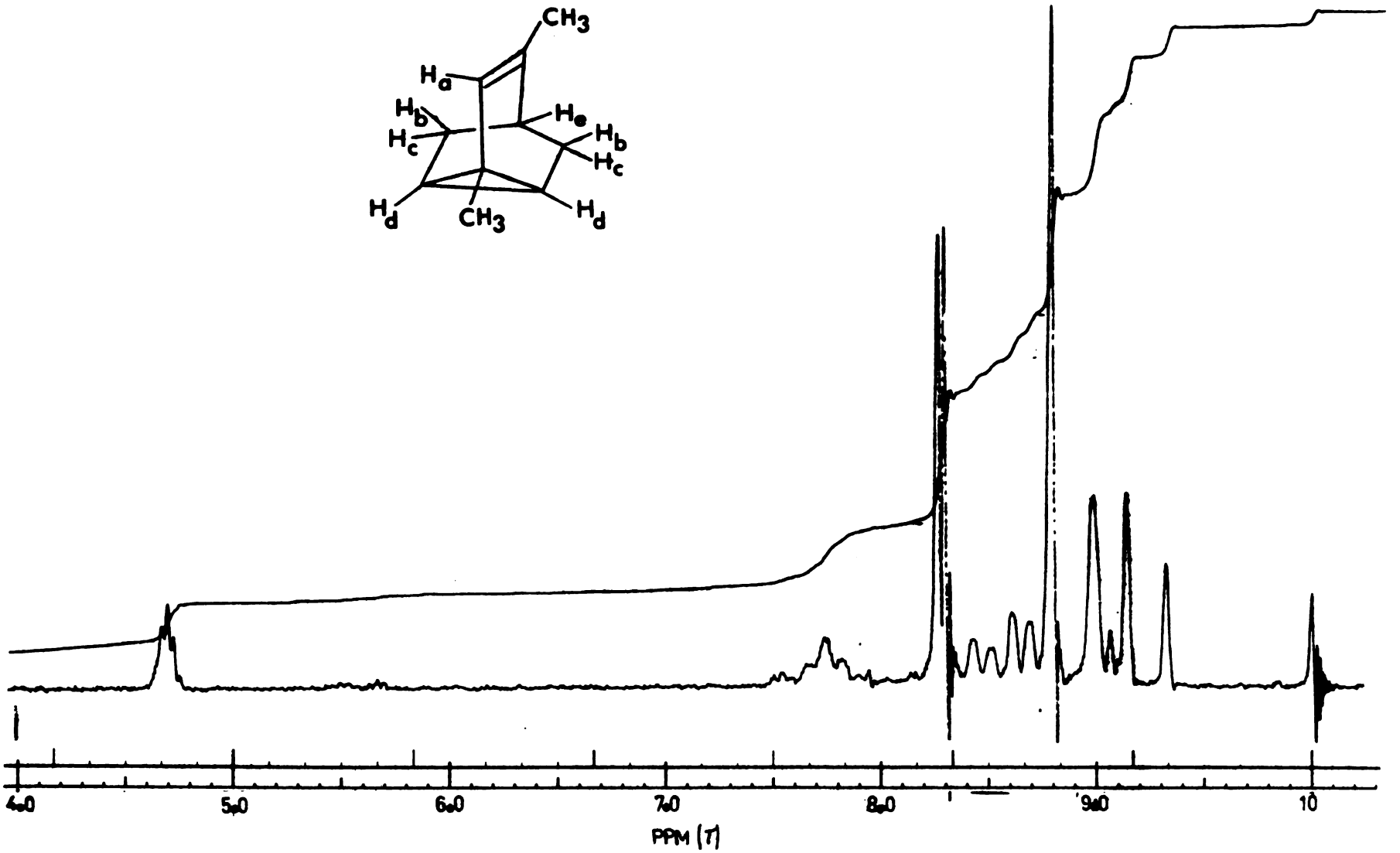
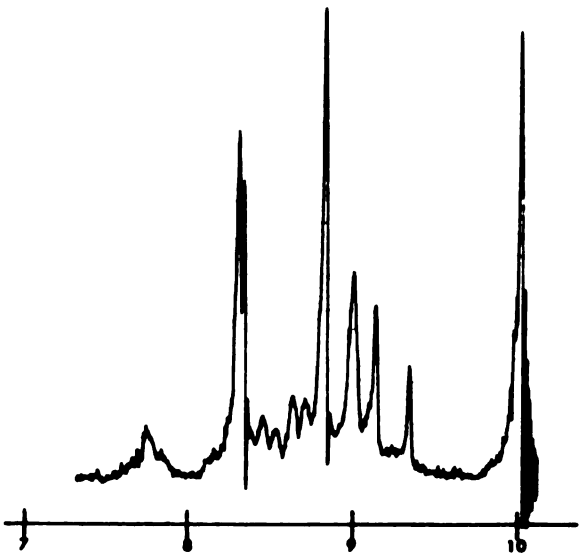
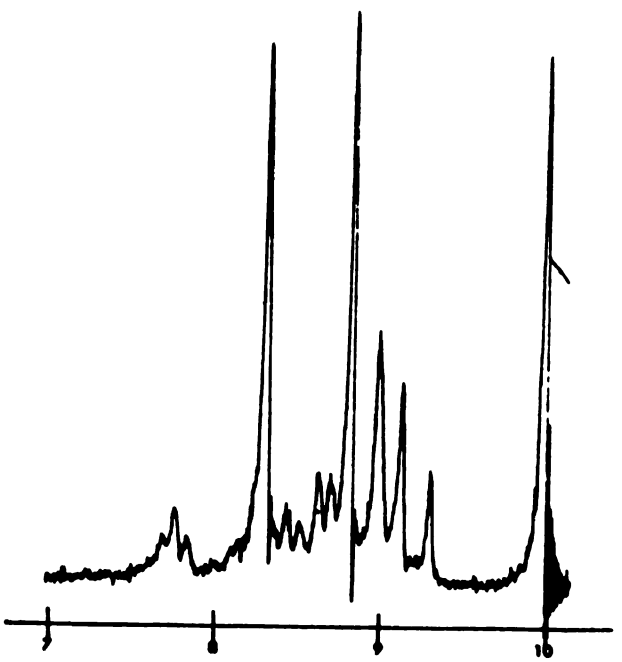


Figure 5. Nmr Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene (XI)

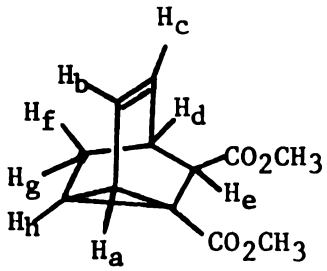


a) Before irradiation of signal due to H_a



b) After irradiation of signal due to H_a

Figure 6. Double Resonance Data of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]-oct-3-ene



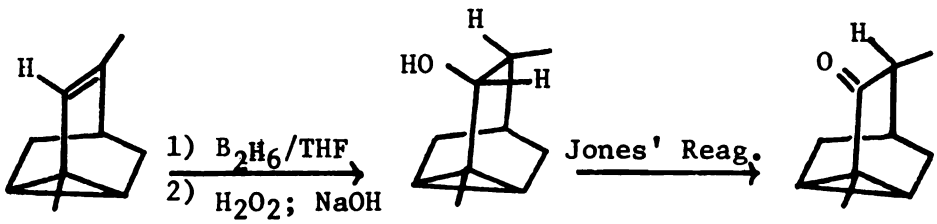
XII

H_a, H_d	7.75--7.35 τ	(complex)	
H_b	4.08 τ	(multiplet)	J = 8.2 cps
H_c	4.38 τ	(multiplet)	J = 8.2 cps
H_e	6.80 τ	(doublet)	
H_f	9.32 τ	(doublet)	J = 11.5 cps
H_g	8.56 τ	(multiplet)	J = 2.5 cps
H_h	8.21 τ	(multiplet)	J = 2.5 cps

Figure 7. Nmr Assignment of Compound XII

Both XI and XI′ have a plane of symmetry which should render this compound optically inactive. Experimental confirmation of this fact was obtained by measurements of the optical rotation at five different wavelengths.

A choice between structures XI and XI′ was finally made by the following procedure. The olefin was converted to the alcohol XIII by a hydroboration-oxidation sequence, care being taken to avoid cyclopropane ring opening and subsequent diol formation [18] (Figure 8). The structure XIII, assigned according to the expected



XI XIII XIV

Figure 8. Conversion of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene to the Corresponding Alcohol (XIII) and Ketone (XIV)

anti-Markownikoff cis-addition of diborane to the double bond, is supported by infrared absorption at 3375 cm^{-1} (Figure 9); the appearance of a weak molecular ion at m/e = 152 and a major ion at M-18 in the mass spectrum (Figure 10); and a hydroxyl hydrogen signal at 5.6--5.8 τ in the nmr, as evidenced by a deuterium exchange experiment.

Oxidation of XIII with Jones' reagent yielded a ketone (XIV) having a carbonyl absorption at 1740 cm^{-1} in the infrared spectrum (Figure 11); a molecular ion at m/e = 150 in the mass spectrum (Figure 12); and nmr absorptions (Figure 13) at 8.2--8.3 τ (cyclopropyl methyl) and 8.7--8.9 τ (C-4 methyl). The quartet at 6.4--6.8 τ is due to the splitting of H_a by the adjacent methyl group, and protons H_c and H_d give rise to the broad signal in the region 7.4--8.0 τ. Protons H_b again show the highest field absorption (9.0 τ); whereas the low field signal appearing at 4.6--4.9 τ apparently comes from H_e. The unusually large chemical shift of H_e caused some concern as to whether the signal actually originated from XIV or from the presence of an impurity. Vpc analysis (DEGS and SE-30 analytical columns) showed no appreciable impurities. A 2,4-dinitrophenylhydrazone derivative was made and nmr analysis of this in deuterochloroform showed the same signal at 4.2 τ. The methyl groups appeared at 8.1 and 8.5--8.7 τ; the H_a quartet at 5.9--6.4 τ; the H_b signal at 8.7--8.9 τ; and the H_c and H_d signals at 7.2--7.6 τ. The aromatic hydrogens of the DNP absorbed at 2.3 and 2.8 τ.

The conjugation of the carbonyl function in XIV with the three membered ring was demonstrated by the characteristic ultra-

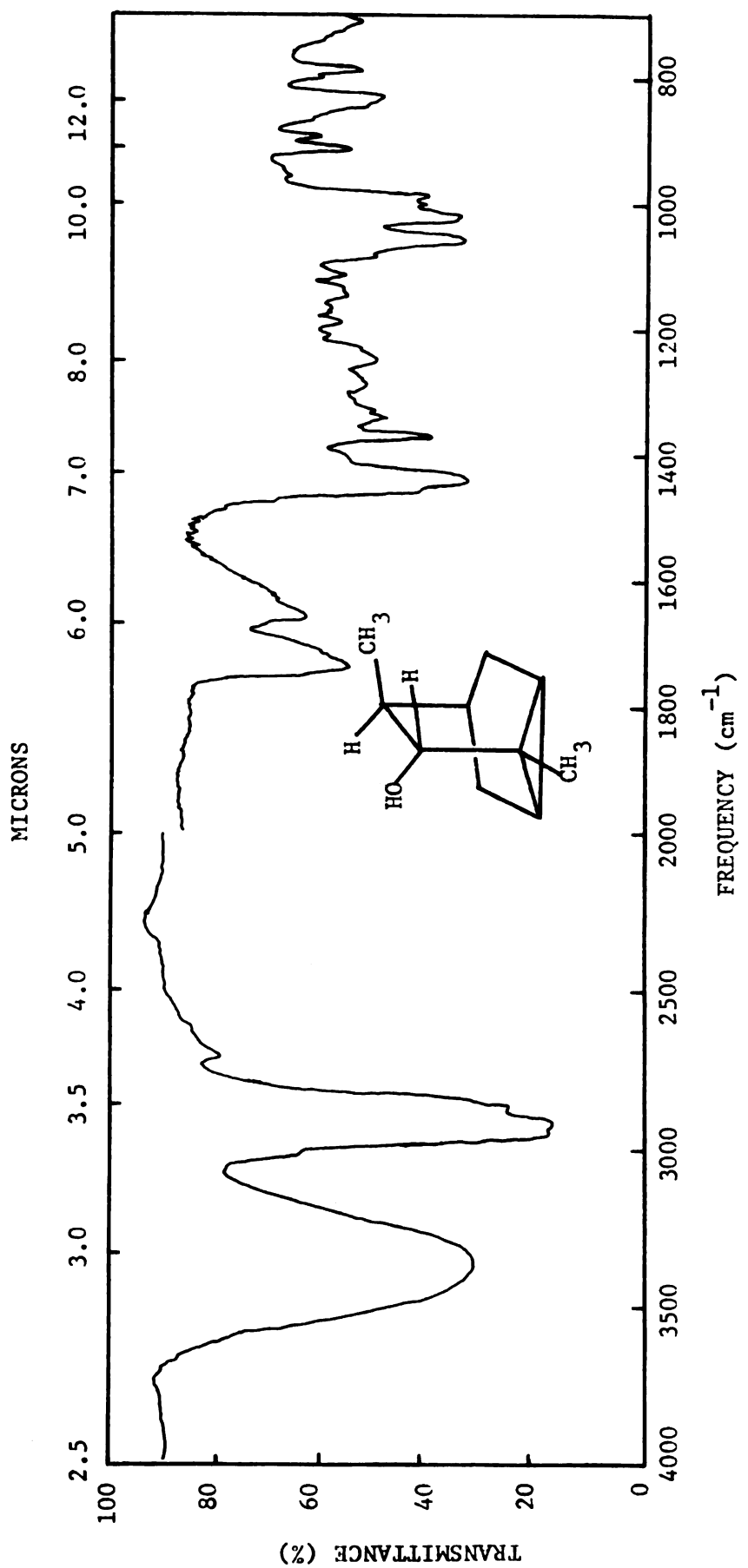


Figure 9. Infrared Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-ol (XIII)

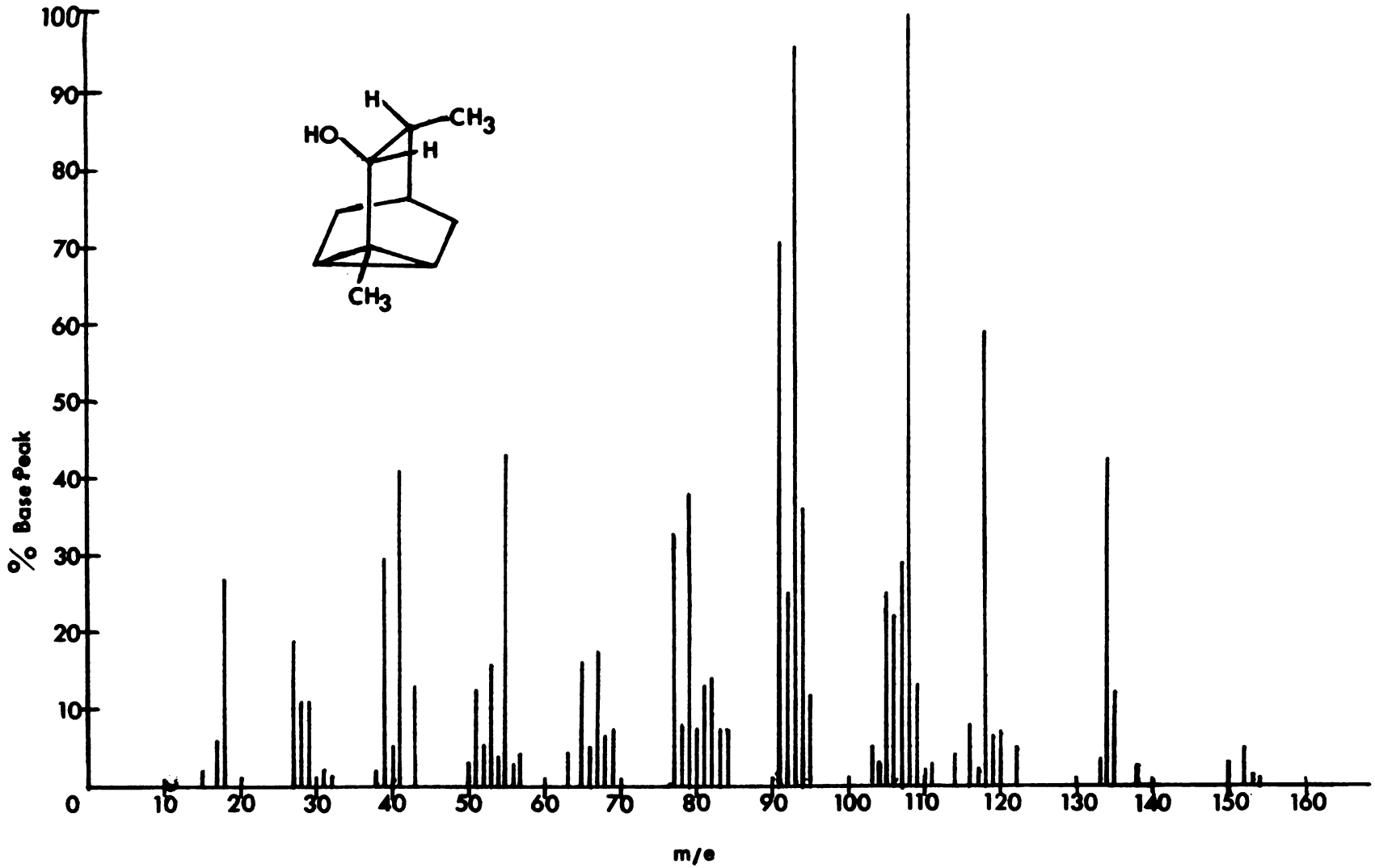


Figure 10. Mass Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-ol (XIII)

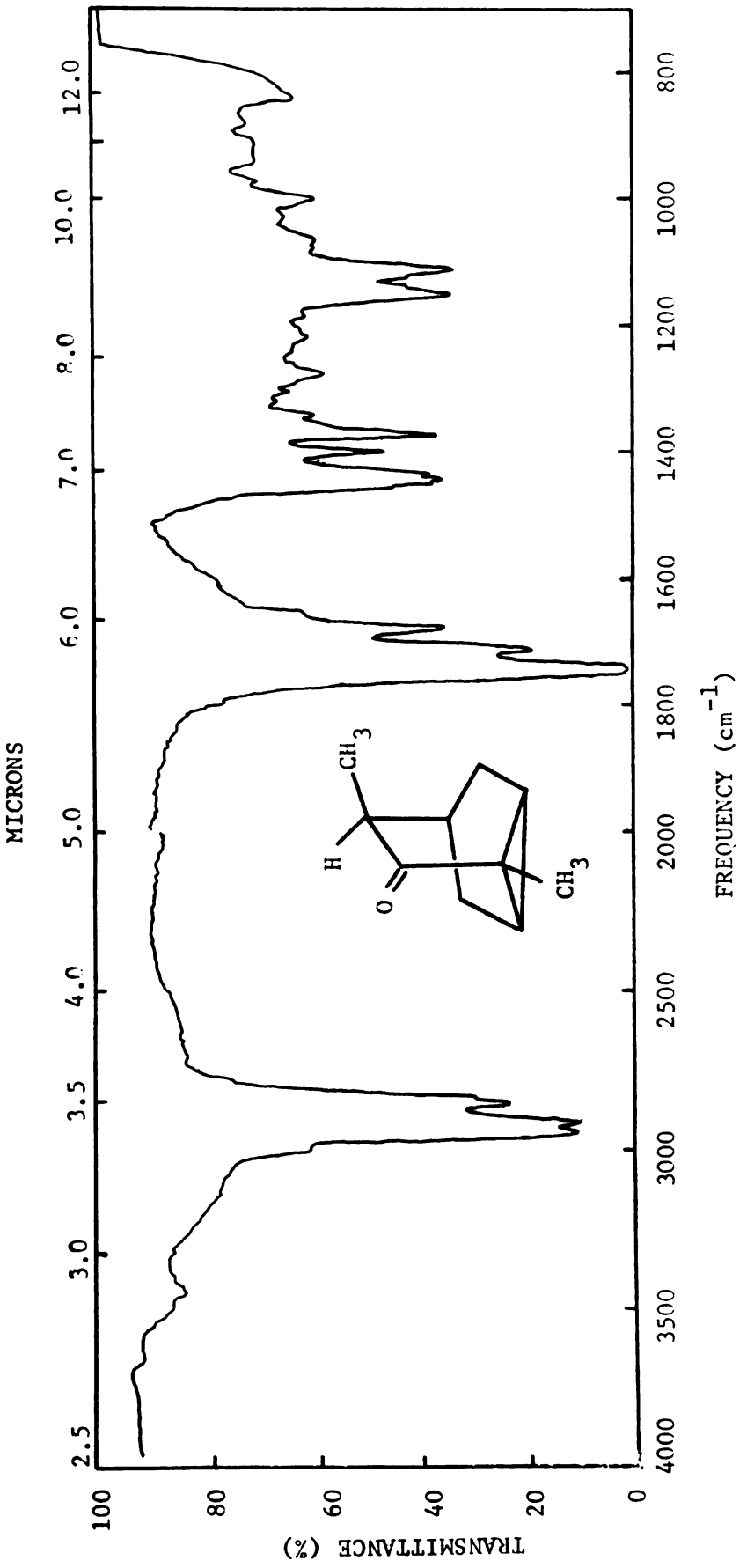


Figure 11. Infrared Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (XIV)

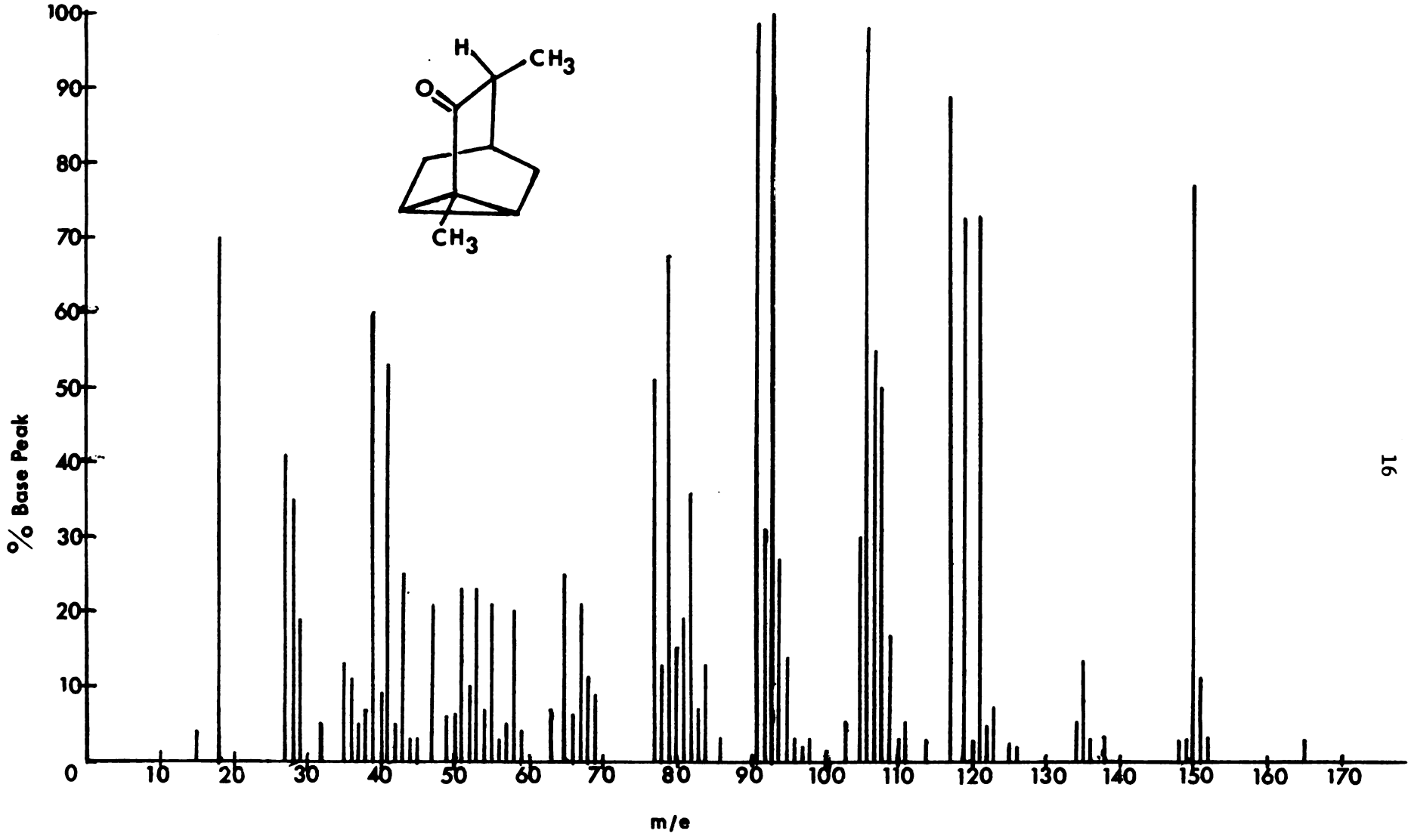


Figure 12. Mass Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (XIV)

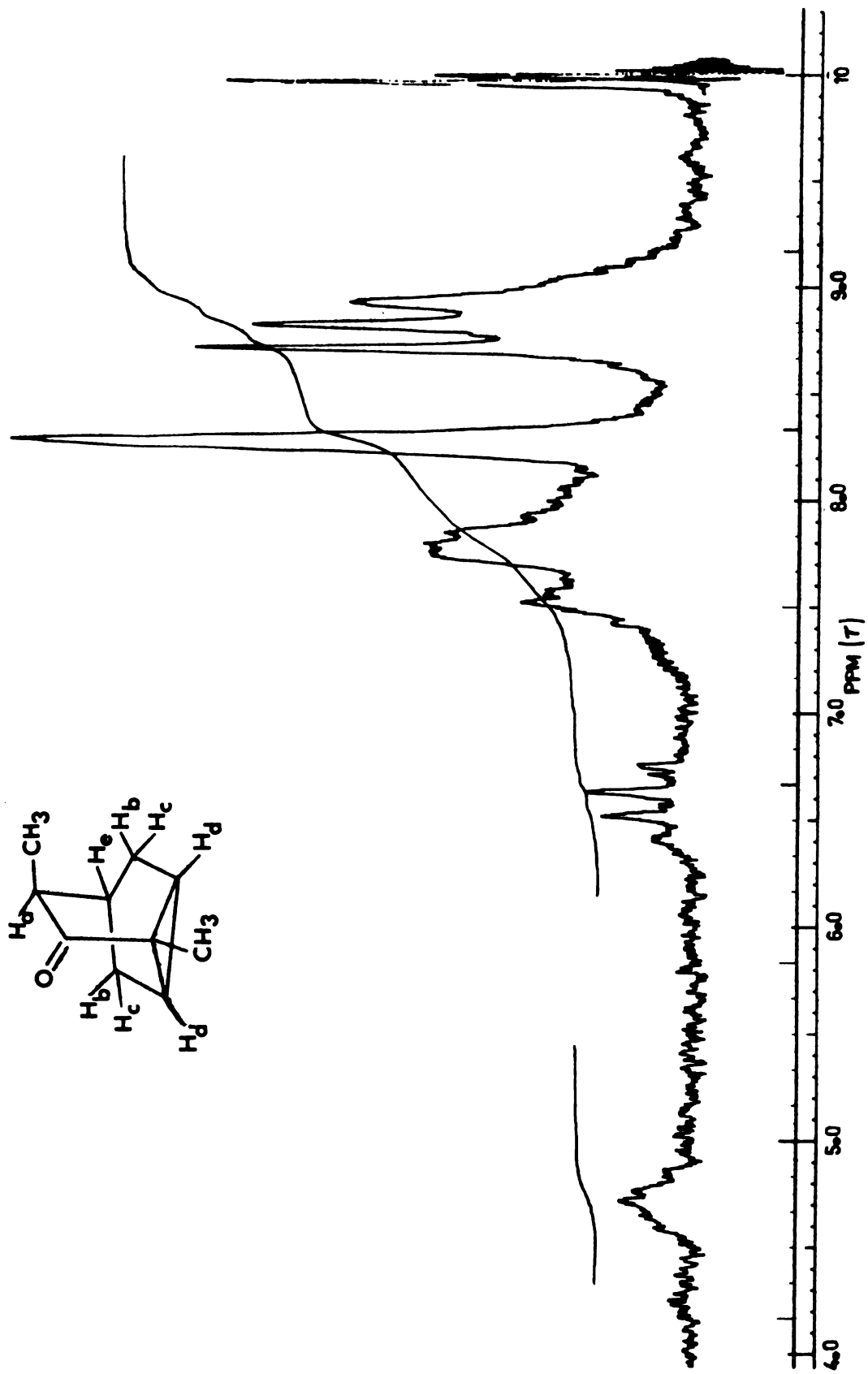


Figure 13. Nmr Spectrum of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (XIV)

violet absorption at $\lambda_{max}^{ethanol}$ = 209 mμ (log ε = 3.50). This fixes the location of the carbonyl group at C-3 and conclusively establishes structure XI (methyl group at C-4) for the olefinic solvolysis product.

In order to determine what effect, if any, the two methyl groups may have on this reaction, the silver ion assisted rearrangement of 3-nortricyclylcarbinyl bromide (XV) in acetone was studied. Preparation of XV was accomplished by the two methods outlined in Figure 14: 1) reaction of 3-nortricyclylcarbinol (XVI) with phosphorus tribromide or 2) preparation of the tosylate or brosylate derivatives of XVI and subsequent displacement with lithium bromide in dimethylformamide.

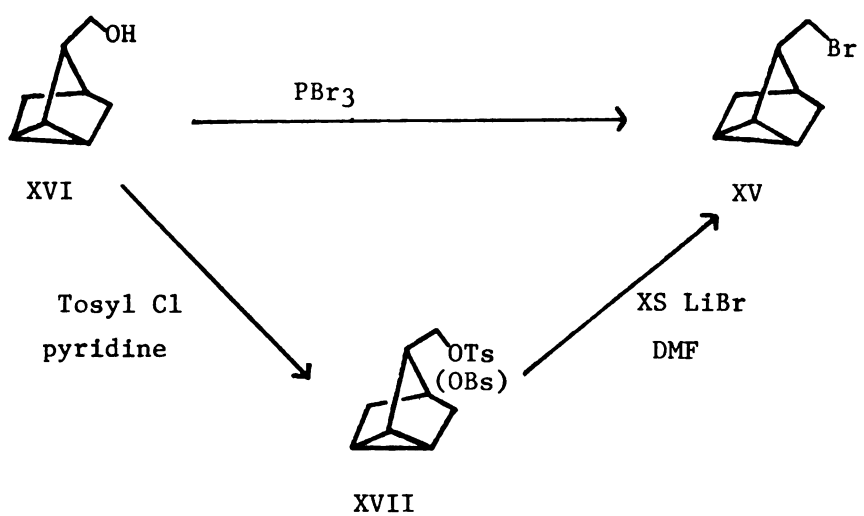


Figure 14. Preparation of 3-Nortricyclylcarbinyl Bromide (XV)

From the reaction of XV with wet silver perchlorate in acetone, three products were isolated by preparative vpc (SE-30 column, 3/8" x 20') in a ratio of 1:4:1 (Figure 15). The first component

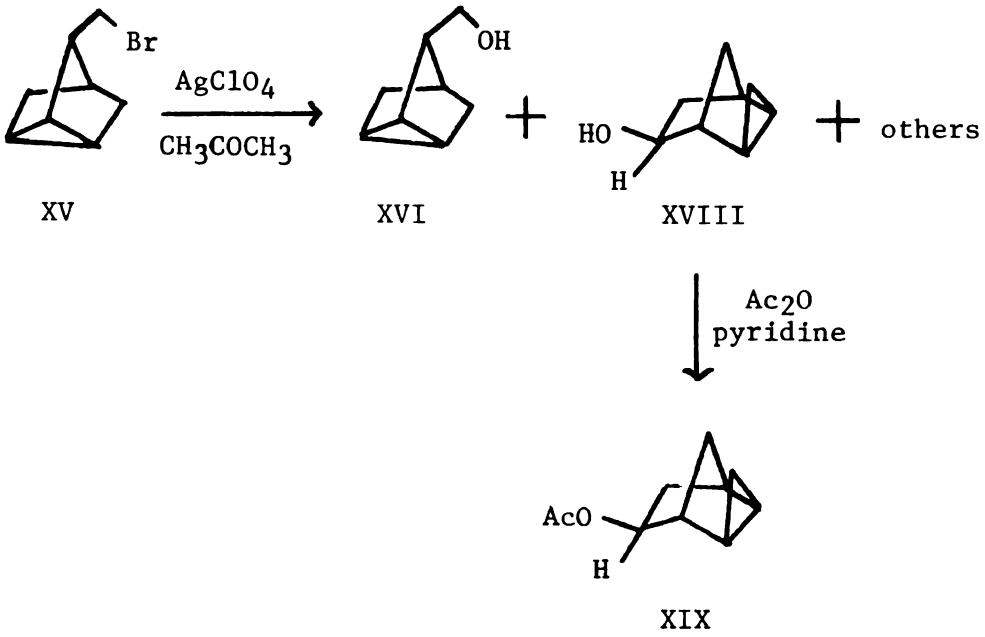


Figure 15. Reaction of 3-Nortricyclylcarbinyl Bromide with Silver Perchlorate

was not identified; the second was shown to be alcohol XVIII by a comparison of the corresponding nmr and infrared spectra with authentic copies provided by Professor R. R. Sauers.[4] The third reaction product was similarly shown to be the alcohol XVI.

It was further demonstrated that the major product formed in the reaction of XV with silver perchlorate in glacial acetic acid rather than acetone was, in fact, identical to the acetate produced by the action of acetic anhydride in anhydrous pyridine on XVIII.

The different kinds of products obtained from the silver ion assisted solvolyses of I and XV (an olefin in the first case and an alcohol in the second) suggest, at first glance, that two different mechanisms are operating in these reactions. Two possible reaction paths are outlined in Figure 16.

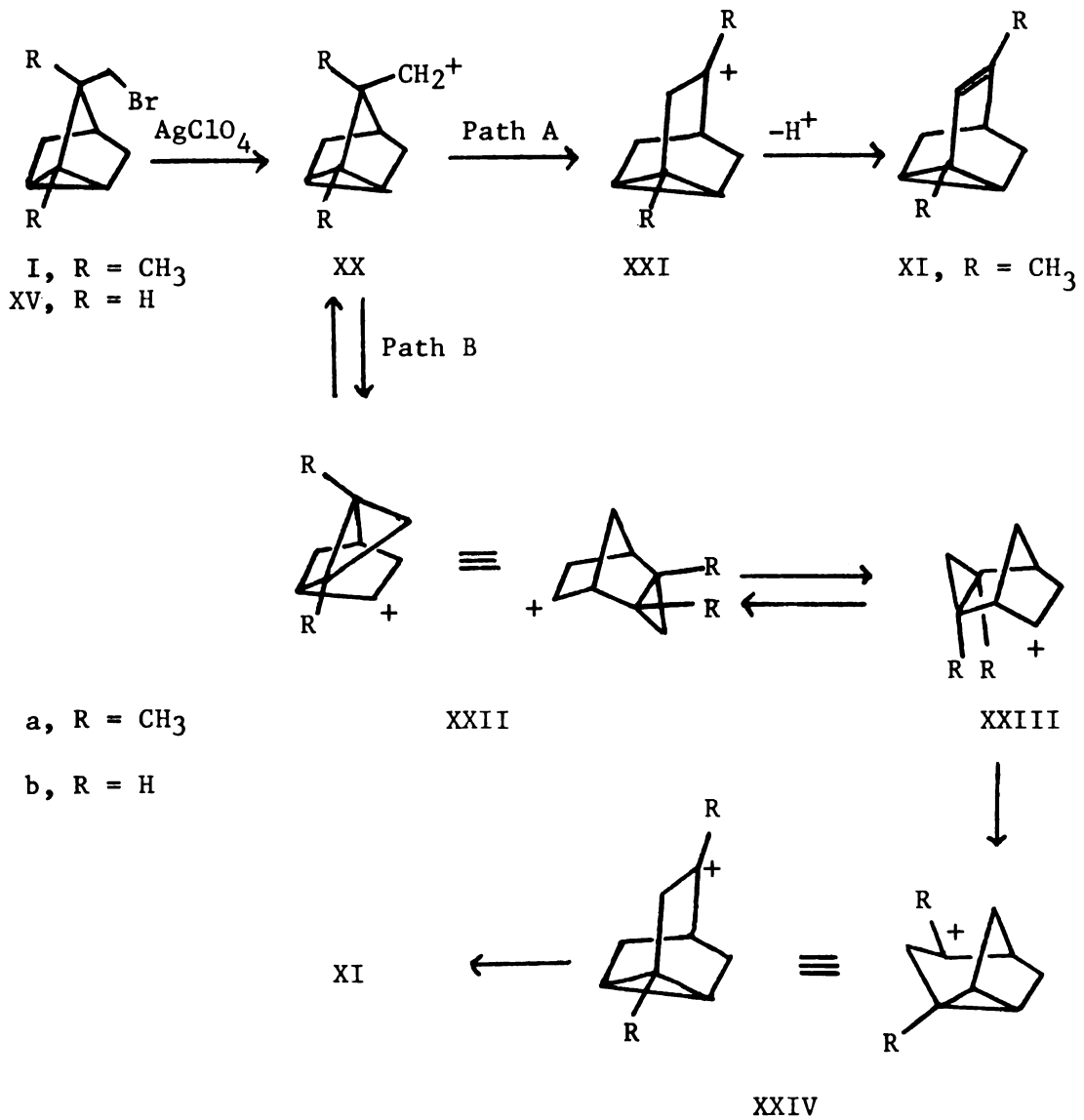


Figure 16. Reaction Paths for the Silver Ion Assisted Solvolyses of π-Bromotricyclene and 3-Nortricyclylcarbinyl Bromide

The studies of Sauers, Beisler, and Feilich[4] and those of Berson et al.[6,19,20] support Path B for the formation of alcohols derived from ions XXIIb and XXIIIb in the 3-nortricyclylcarbinyl system. Although the rearrangement of XXIIIb to XXIVb occurs to a small extent in this system, the reverse of this rearrangement does

not assume any significance.

In the dimethyl substituted tricyclylcarbinyl system (I → XI), Path A is more probable than in the previous case because of the very favorable rearrangement of the primary carbonium ion XXa to the tertiary cation XXIa. Likewise, ion XXIVa is stabilized relative to XXIVb by the presence of the methyl groups which serve to localize the positive charge on C-4, thereby making the conversion of XXIIIa to XXIVa more exothermic and probably faster than in the 3-nortricyclylcarbinyl system.

Since the system is rigid and free of conformational interconversions, the methyl groups cannot significantly distort the geometry of the ring and thus destroy the orientation of the cyclopropane orbitals with the cationic center (Figure 17). This cation

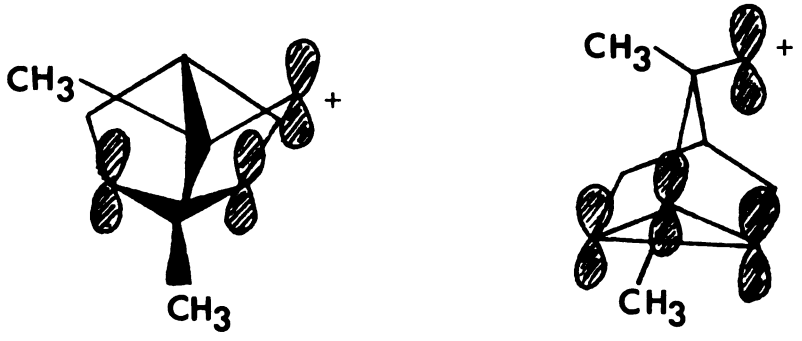


Figure 17. Geometry of the Cation Derived from π-Bromotricyclene

possesses the geometry discussed by Berson as necessary for cyclopropane participation.[6,20] Furthermore, the p-orbitals of the cyclopropane ring are pointed nearly directly at the cationic center and overlap can occur efficiently with both ends of the cyclopropyl bond, allowing "normal" cyclopropane participation to occur.

This orientation of the orbitals has recently been shown to be a necessary condition for activity in cyclopropane participation by Haywood-Farmer and Pincock in their investigations into the solvolysis of 8-tricyclo[3.2.1.$0^{2,4}$]octane derivatives.[21]

Although the experimental results reported here do not permit a clear choice between the mechanisms described in Figure 16: the simplest interpretation would employ the common pathway, Path B, as the most likely for these reactions.

EXPERIMENTAL

I. General Procedures

A. Spectra

Infrared spectra were obtained on a Perkin-Elmer 237B Grating Infrared Spectrophotometer. Sodium chloride cells or discs were used for all determinations.

Ultraviolet and near infrared spectra were measured using 1 cm. quartz cells on a Cary 14 recording spectrophotometer.

Nuclear magnetic resonance spectra were determined on a Varian A-60 high resolution spectrometer with tetramethylsilane as a standard. Double resonance experiments employed a JEOLCO C-60-H high resolution instrument.

Mass spectra were obtained using a Hitachi RMU-6-E mass spectrometer.

B. Gas Chromatography

Preparative vapor phase chromatography was accomplished with an Aerograph A-90-3P gas chromatograph. Analytical chromatographic analyses employed a Varian Series 1200 Aerograph. Relative peak areas were determined by the triangulation method.

C. Microanalysis

All microanalytical data were obtained from the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

D. Melting Points

Melting points were determined on either a Reichert hot-stage or a Thomas Unimelt capillary melting point apparatus. All temperatures are uncorrected and recorded in Centigrade degrees.

II. Synthesis of π-Bromotricyclene (I)

A. α-Bromocamphor (VII)

A 152 g (1 mole) sample of dl-camphor in a three-neck flask equipped with a mechanical stirrer and condenser was heated on a steam bath while 116 g (1 mole, 53 ml) of bromine was slowly added. After the evolution of hydrogen bromide ceased (signaled by a clearing of the reaction mixture), the resulting light amber colored solution was stirred for two hours and then poured into cold water containing a few grams of sodium bisulfite. The resulting solid was filtered, dried by pressing between paper toweling, and stored in a dessicator. All attempts at recrystallization failed.[22] The crude material melted at 50--52° and the yield of α-bromocamphor was essentially quantitative.

B. α,π-Dibromocamphor (VIII)

A 1000 ml three-neck flask containing 184 ml of chlorosul-

fonic acid and 116 g of bromine and equipped with a condenser, mechanical stirrer, and a thermometer was cooled to below 10^{o} in an ice bath. Then 231 g (1 mole) of α-bromocamphor was added with stirring, maintaining the temperature between 25^{o} and 30^{o}. The mixture was allowed to stir for five to six hours at room temperature. After reaction was complete the contents of the flask was poured into an ice-water mixture and stirred until the product became grannular or nearly so. Solid sodium bisulfite was added to decompose any excess bromine. The precipitate was filtered, washed with water, 5% sodium hydroxide, and again with water. After one recrystallization from 95% ethanol 152 g of α,π-dibromocamphor melting at 139--141^{o} was obtained. This corresponded to a 50% yield based on dl-camphor.

C. π-Bromocamphor (IX)

The α,π-dibromocamphor (152 g) obtained in the previous step was dissolved in 600 ml of methylene chloride and placed in a three-neck flask fitted with a mechanical stirrer, thermometer, and hydrogen bromide gas inlet system. To this was added 104 g of activated zinc powder[23] and hydrogen bromide was allowed to bubble through the reaction mixture for at least four hours. The mixture was then filtered and the methylene chloride solution washed with water, dried ($MgSO_4$), and distilled to remove the solvent. The resulting solution was cooled to 0^{o} (freezer of a refrigerator) and the solid π-bromocamphor was collected and recrystallized from hexane to yield a product melting at 91--95^{o}. A total of 59 g was

obtained (53%).

D. π-Bromocamphor Hydrazone (X)

To prepare the hydrazone, 59 g of the ketone was refluxed for six hours with 130 ml (4 moles) of 95% hydrazine and 63 ml (1 mole) of acetic acid in 200 ml of 95% ethanol. After refluxing, the reaction mixture was allowed to cool and the ethanol was removed at aspirator pressure. The mixture was brought to near its original volume with ether, the lower hydrazine layer was removed, and the upper layer was washed with 10% sodium hydroxide saturated with sodium chloride once and with saturated sodium chloride solution three times. Removal of the ether at aspirator pressure yielded 63 g of the hydrazone.

E. π-Bromotricyclene (I)

The hydrazone X (63 g) was immediately dissolved in 110 ml of ethanol in a three-neck flask equipped with a condenser and a mechanical stirrer. Yellow mercuric oxide (88 g) was slowly added and the mixture was refluxed and stirred overnight. After filtering, the reaction mixture was carefully distilled to remove the ethanol.[13] An equal volume of cold water was added to the solution remaining in the distillation flask and the mixture was extracted four times with pentane, The pentane extracts were dried ($MgSO_4$) and the solvent was carefully removed to yield 38 g of π-bromotricyclene (69%). Distillation at aspirator pressure gave material boiling at 112° with $n_D^{25°} = 1.5076$. Infrared analysis showed bands at 3050 cm^{-1}, 1250 cm^{-1}, and 875--800 cm^{-1}, characteristic of the cyclopropyl

carbon - hydrogen, the carbon - bromine bond, and the tricyclene system, respectively (Figure 18).

III. Reaction of π-Bromotricyclene with Silver Perchlorate

To a stirred solution of 15 g of π-bromotricyclene in 50 ml of acetone was carefully and dropwise added 14 g of silver perchlorate, prepared from the action of 5.3 ml of perchloric acid on excess silver oxide (10--14 g). The reaction vessel was stoppered, wrapped in aluminum foil, and allowed to stand for 72 hrs at room temperature with stirring. The reaction mixture was then filtered, care being taken to cool the filtrate because of extreme volatility of the product. To the filtrate was added 20% sodium chloride solution until cessation of precipitation; the solution was refiltered, the filtrate was treated with 20% sodium hydroxide until basic, and the resulting solution was extracted four or five times with ether. The ether extracts were dried ($MgSO_4$), most of the solvent was removed by distillation, and the remaining mixture was separated by vapor phase chromatography (20% SE-30 preparative column. Vpc yield of 2,4-dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene (XI) was 41.8%.

IV. Hydroboration-Oxidation of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]-oct-3-ene (XI)

To the hydroboration flask (25 ml round-bottom flask with a septum inlet and equipped with a 3-way stopcock connected to a

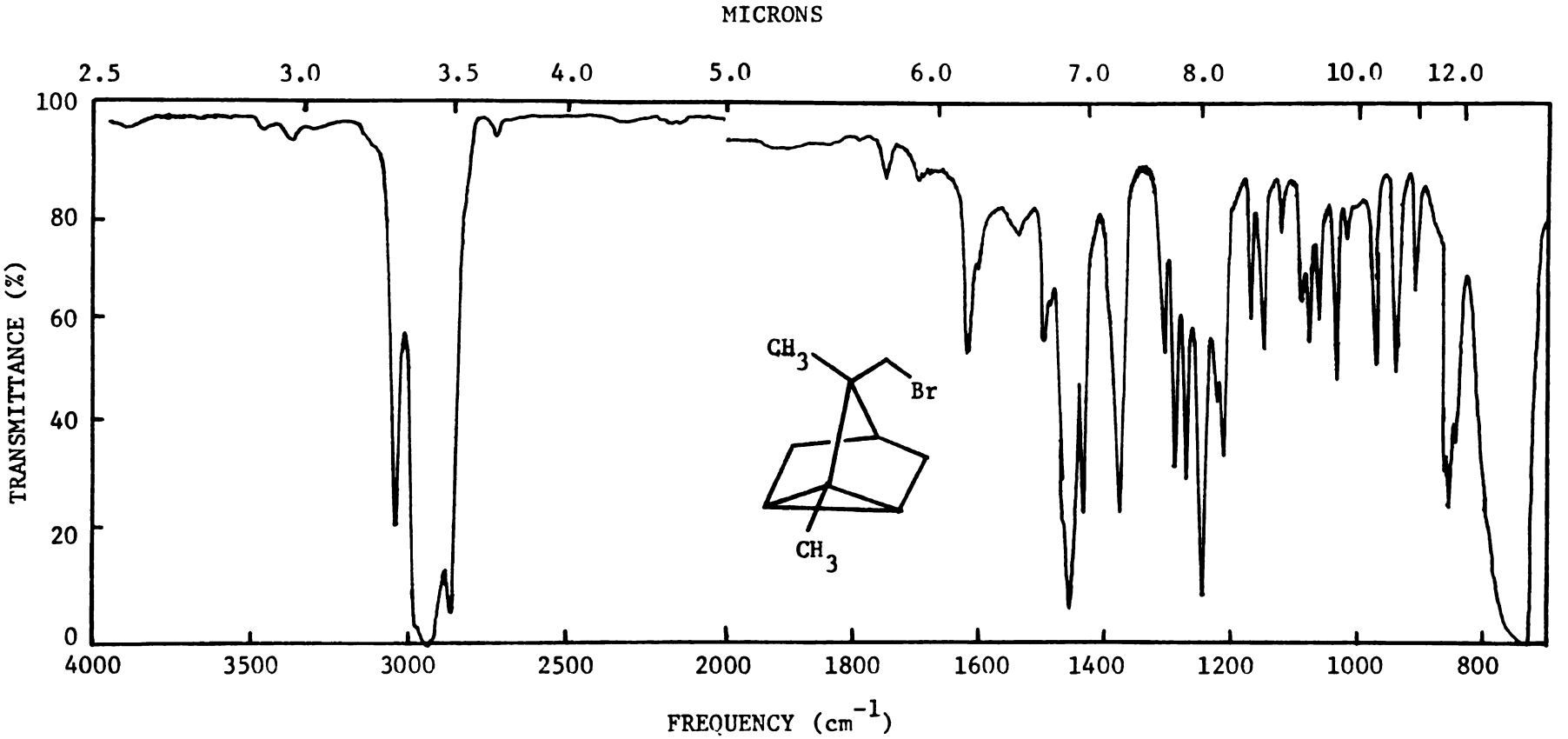


Figure 17. Infrared Spectrum of π-Bromotricyclene (I)

nitrogen gas inlet and a mercury bubbler) were added 0.3 g (22 mmoles) of XI and 6 ml of tetrahydrofuran. The flask was cooled in an ice-water bath and 5 ml of BH_3·THF was added dropwise with stirring through the septum inlet over a 15--20 minute period. The carefully cooled reaction mixture was left to stir for 90 minutes. Oxidation of the dialkylborane was accomplished by the careful addition of 4.2 ml of 3 N sodium hydroxide followed by 3 ml of 30% hydrogen peroxide, after which the flask and contents were allowed to stand at room temperature for 60 minutes. Solid potassium carbonate was then added to the reaction mixture with stirring until crystallization began. The layers were separated and the alcohol was separated from the THF layer by vpc (DEGS analytical column).

V. Oxidation of 2,4-Dimethyltricyclo[3.2.1.$0^{2,7}$]-octan-3-ol (XIII)

The alcohol, XIII, was dissolved in reagent grade acetone in an Ehrlenmeyer flask and solution of Jones' reagent was added with stirring until an orange color persisted for at least 15 minutes. The solution was decanted, washed with acetone, and a few drops of iso-propyl alcohol were added. Solid sodium bicarbonate was then added with stirring until the solution became neutral, after which stirring was continued for 30 minutes. The precipitated salts were filtered off, the solvent was removed, water was added to the contents of the flask, and the resulting solution was extracted with ether. After drying ($MgSO_4$), the ether was removed to yield 2,4-dimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (XIV). The mass

spectrum (Figure 12) gave %(P+1) = 14.3, %(P+2) = 3.9 (theoretical P+1 = 11.0%, P+2 = 0.75%). A 2,4-DNP was prepared and crystallized as dark orange needles, m.p. 108 - 110°.

Calcd.	53.8% C; 5.4% H; 16.1% N
Anal.	53.82% C; 5.36% H; 16.05% N

VI. Synthesis of 3-Nortricyclylcarbinyl Bromide (XV)

A. 3-Nortricyclylcarbinyl Tosylate (XVII)

A solution of 2.8 g of 3-nortricyclylcarbinol in 50 ml of dry pyridine in a glass stoppered Erhlenmeyer flask was cooled to 0° and treated with a 1 molar excess of tosyl chloride. After complete dissolution, the flask and contents were refrigerated until formation of yellow-brown pyridinium hydrochloride was observed. After cessation of precipitation the mixture was poured with stirring into an ice-water mixture. The oily product was extracted with ether, and the extracts were washed with 1:1 hydrochloric acid and dried (K_2CO_3, Na_2SO_4). Evaporation of the ether and crystallization from a 50:50 mixture of ethyl acetate and pentane gave a greater than 90% yield of the tosylate. The infrared spectrum showed the characteristic bands at 1375 cm^{-1} and 1175 cm^{-1}.

B. 3-Nortricyclylcarbinyl Bromide (XV)

To a stirred solution of approximately 3 g of lithium bromide (a three-fold excess) in acetone was added 1.2 g of 3-nortricyclylcarbinyl tosylate. The mixture was allowed to stir at room temperature for 3 days before the tosylate salt was filtered

off. The filtrate was then washed with water to remove excess lithium bromide and the acetone was removed by distillation. Extraction of the distillation residue with chloroform and careful distillation yielded the bromide in quantitative amounts.

VII. Reaction of 3-Nortricyclylcarbinyl Bromide with Silver Perchlorate

To a stirred solution of 0.6 g of the bromide XV in 10 ml of acetone was added a solution of 1.2 g of silver oxide in 0.4 ml of perchloric acid. The mixture was left to stir at room temperature for 72 hrs and worked up as described in the reaction of π-bromotricyclene with silver perchlorate. Collection of the reaction products in carbon tetrachloride from a 20% SE-30 preparative column yielded compounds XVI and XVIII in a 1:4 ratio.

VIII. Acetolysis of 3-Nortricyclylcarbinyl Bromide

A solution of 1.0 g of silver oxide in 0.5 ml of perchloric acid was added dropwise to a solution of 0.5 g of the bromide XV in 10 ml of glacial acetic acid and left for two days. Work up as previously described gave XIX as the major product.

IX. Formation of Acetate XIX

Alcohol XVIII was converted into its acetate by reaction of the alcohol with 1 ml of acetic anhydride in 2--5 ml of anhydrous pyridine. The reaction mixture was allowed to stand a few

hours, then it was poured into an ice-water slush and extracted with ether. Most of the ether was removed by distillation and the final product (XIX) was collected from a 20% SE-30 preparative vpc column.

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