THE SYNTHESIS OF TETRACYCLO [4.3.0.0.^{2,4}0.^{3,7}]NONA-8-ENE

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

James D. Slee

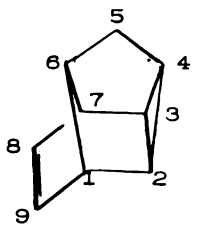
1966

ABSTRACT

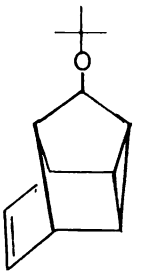
THE SYNTHESIS OF TETRACYCLO[4.3.0.0.^{2,4}0.^{3,7}]NONA-8-ENE

by James D. Slee

The synthesis of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (I) was undertaken to serve as a model for the preparation of 5-(t-butoxyl)-tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (II).

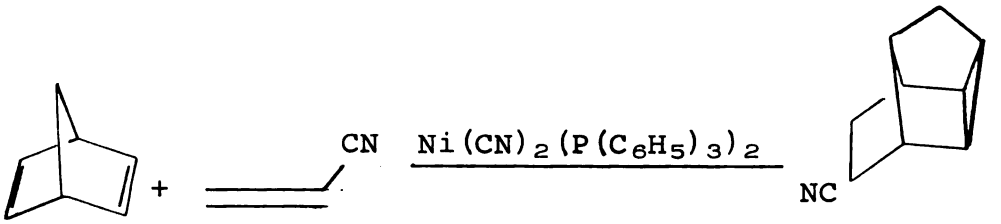


(I)



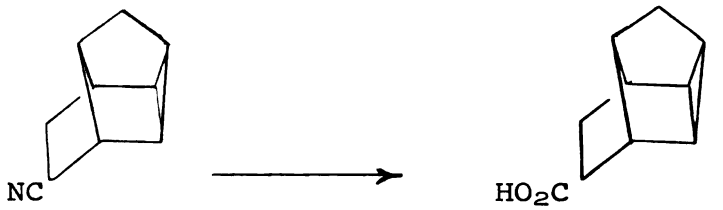
(II)

The first step in the synthesis employed a pseudo Diels-Alder reaction of norbornadiene (III) with acrylonitrile (IV) in the presence of dicyanobis (triphenylphosphine) nickel (II) to form 8-cyanotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (V).[1]



(III) (IV) (V)

Hydrolysis of the nitrile V under alkaline conditions followed by acidification gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]-nonane-8-carboxylic acid (VI).

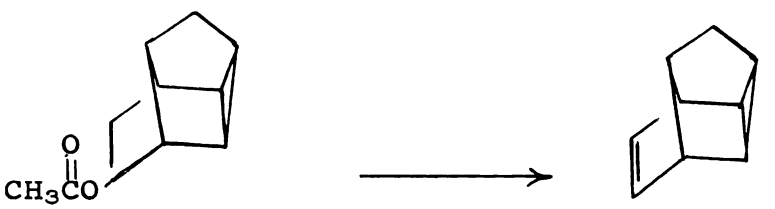


(V) (VI)

Treatment of the acid VI with lead tetraacetate resulted in decarboxylation with the formation of tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate (VII).

[VI] (VII)

Pyrolysis of the acetate VII at 500°C. in a Pyrex column packed with granular silicon carbide gave tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (I) in good yields.



(VII) (I)

REFERENCES

1. G. N. Schrauzer, and Peter Glockner, Ber., 2462 (1964).

THE SYNTHESIS OF TETRACYCLO[4.3.0.0.^{2,4}0.^{3,7}]NONA-8-ENE

By

James D. Slee

A THESIS

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

MASTER OF SCIENCE

Department of Chemistry

1966

ACKNOWLEDGMENT

The author gratefully acknowledges his appreciation to Dr. Eugene LeGoff for his guidance and assistance during the course of this investigation.

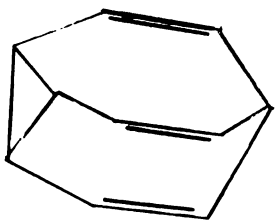
TABLE OF CONTENTS

LIST OF FIGURES

REACTION SCHEMES

INTRODUCTION

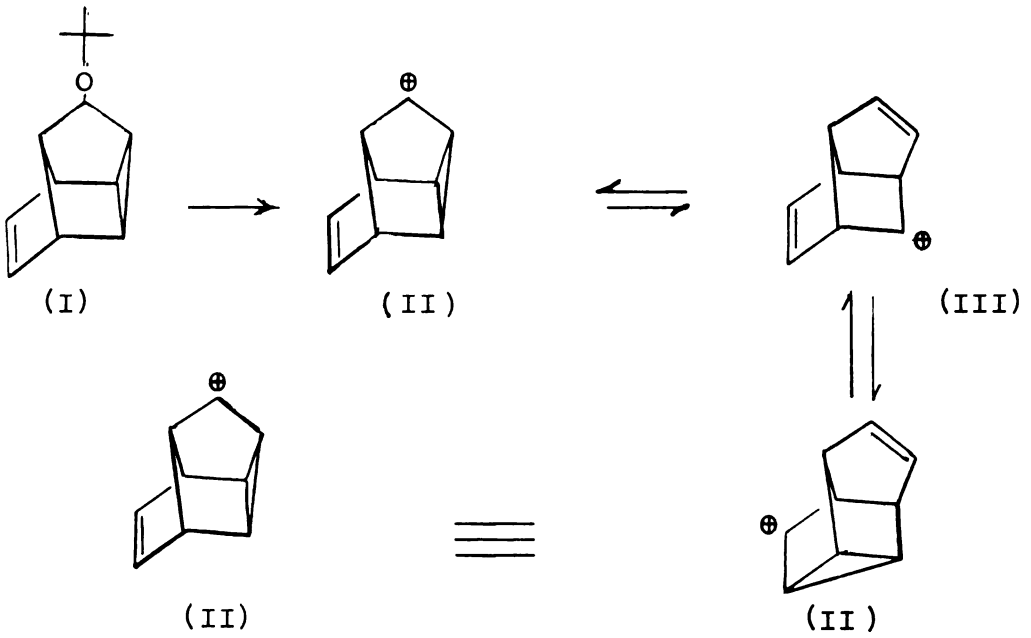
In 1963 Doering proposed a compound in which all isomers should rapidly equilibrate (1). Due to the symmetry of the molecule a single absorption in the nuclear magnetic resonance spectrum should be observed if tautomerism were rapid. This compound, tricyclo[3.3.2.0.^{2,6}]deca-2,7,9-triene, commonly known as bullvalene, was synthesized by Schröder (2). Schröder found that the n.m.r. spectrum at 100^{o} was a singlet corresponding to ten equivalent protons.



Bullvalene

This work suggested the possibility of rapidly equilibrating carbonium ions which should give rise to a simple n.m.r. spectrum. The molecule proposed for the generation of this carbonium

ion was 5-(t-butoxy)-tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (I). Upon treatment with strong acid a homoallylic cyclopropyl carbonium ion II should be generated within this molecule.



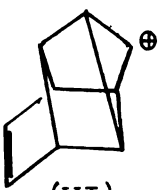
(I) (II) (III)

(II) (II)

The rapid rate at which homoallylic cyclopropyl carbonium ions undergo rearrangement was pointed out by Roberts and Mazur with the acid catalyzed rearrangement of 4-chloromethyl-cyclopropane (3).

Once isomerization occurs to form III a homoallylic carbonium ion may be formed with either of the two double bonds. This type of carbonium ion has been widely investigated from a classical point of view by H. C. Brown (4) and from a nonclassical point of view by S. Winstein (5). Whether the ion is considered classical or nonclassical the fact remains that rearrangement should be rapid.

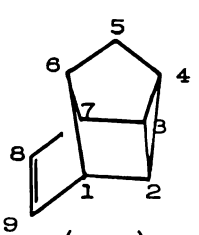
The rearrangement of III gives the original carbonium ion no matter which double bond is involved. By drawing structures for all possible rearrangement products it becomes evident that the original structure is always regenerated. Formation of carbonium ion (VI) has been excluded due to steric requirements of the cyclobutane ring.



(VI)

Because there is only one hydrogen per carbon atom and since the carbonium ion should be stabilized by rapid equilibration, the n.m.r. spectrum may be quite simple. This ion may fall into the category of a spherical non-classical carbonium ion.

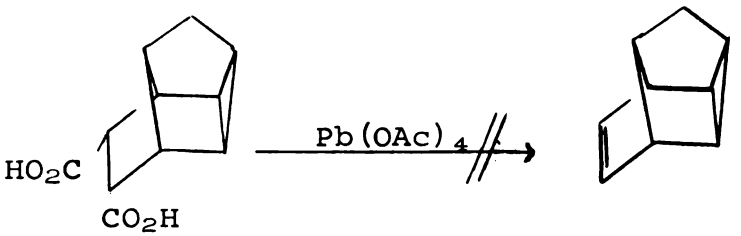
The molecule leading to this carbonium ion has at this time not been synthesized. This work is concerned with the synthesis of a compound which will hopefully serve as a model for the t-butoxy derivative. The model compound is tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (VII).



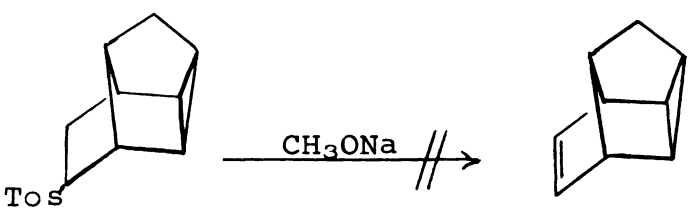
(VII)

Three routes leading to the formation of VII were investigated. The work of van Tamelen and Grob, involving decarboxylations of cis-diacids to form sensitive alkenes, led to the development of the first reaction sequence (6,7,8). It was felt that alkene VII could be obtained by the decarboxylation of the cis-endo-diacid with lead tetraacetate (equation 1). The second reaction sequence involved a tosylate elimination (equation 2). This reaction has been successfully used by Snyder and Soto to form a number of alkenes (9). Finally, an old method, an acetate pyrolysis (10), was proposed (equation 3). Of the three procedures the alkene VII could only be isolated by the third.

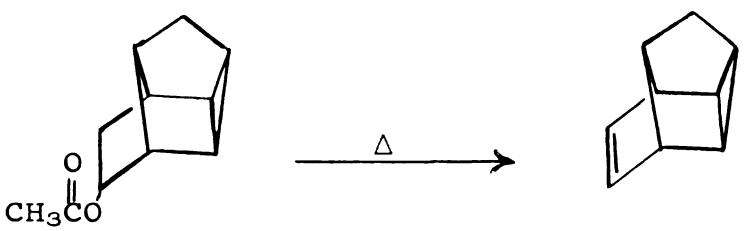
Equation 1



Equation 2



Equation 3



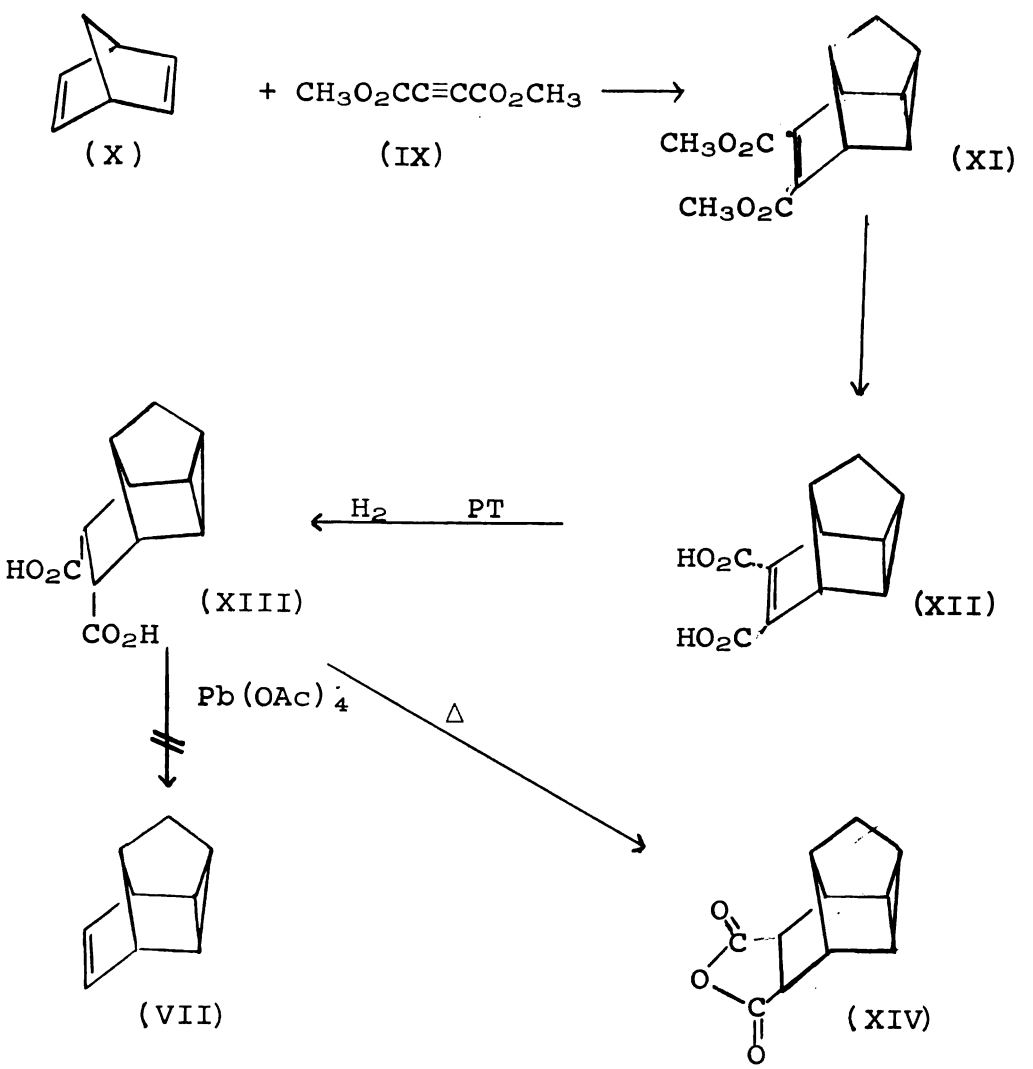
RESULTS AND DISCUSSION

The first attempt to synthesize tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (VII) involved the decarboxylation of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-endo-dicarboxylic acid (VIII) (Scheme I).

The dimethyl ester of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene-8,9-dicarboxylic acid (XI) was readily prepared by heating norbornadiene (X) in the presence of dimethyl acetylenedicarboxylate (IX). Saponification of dimethyl tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene-8,9-dicarboxylate (XI) with aqueous potassium hydroxide followed by acidification with dilute hydrochloric acid led to tetracyclo[4.3.0.0.^{2,4}0,^{3,7}]-nona-8-ene-8,9-dicarboxylic acid (XII).

Reduction of XII by catalytic hydrogenation with Adams' catalyst, reduced platinum oxide, gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-endo-dicarboxylic acid (XIII). The cis-endo-diacid was expected because hydrogenation should occur from the least hindered side of the molecule. Epimerization to the trans acid was unlikely since XIII was not treated with strong acid. This possibility was eliminated by the fact that the trans diacid has been reported and has different properties (11). Chemical evidence that confirmed the cis-endo-diacid was obtained by heating XIII to 220°.

SCHEME I


(X)
+ $CH_3O_2CC{\equiv}CCO_2CH_3$
(IX)
CH_3O_2C
CH_3O_2C
(XI)
H_2 PT
HO_2C
CO_2H
(XIII)
HO_2C
HO_2C
(XII)
$Pb(OAc)_4$
Δ
(VII)
O
C
O
C
O
(XIV)

Dehydration occurred giving tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]-nonane-8,9-endo-dicarboxylic acid anhydride(XIV), mp 118-120^{o} (lit. (11) 120^{o}). An infrared spectrum of XIV showed absorptions at 1850 and 1770 cm^{-1} characteristic of anhydrides.

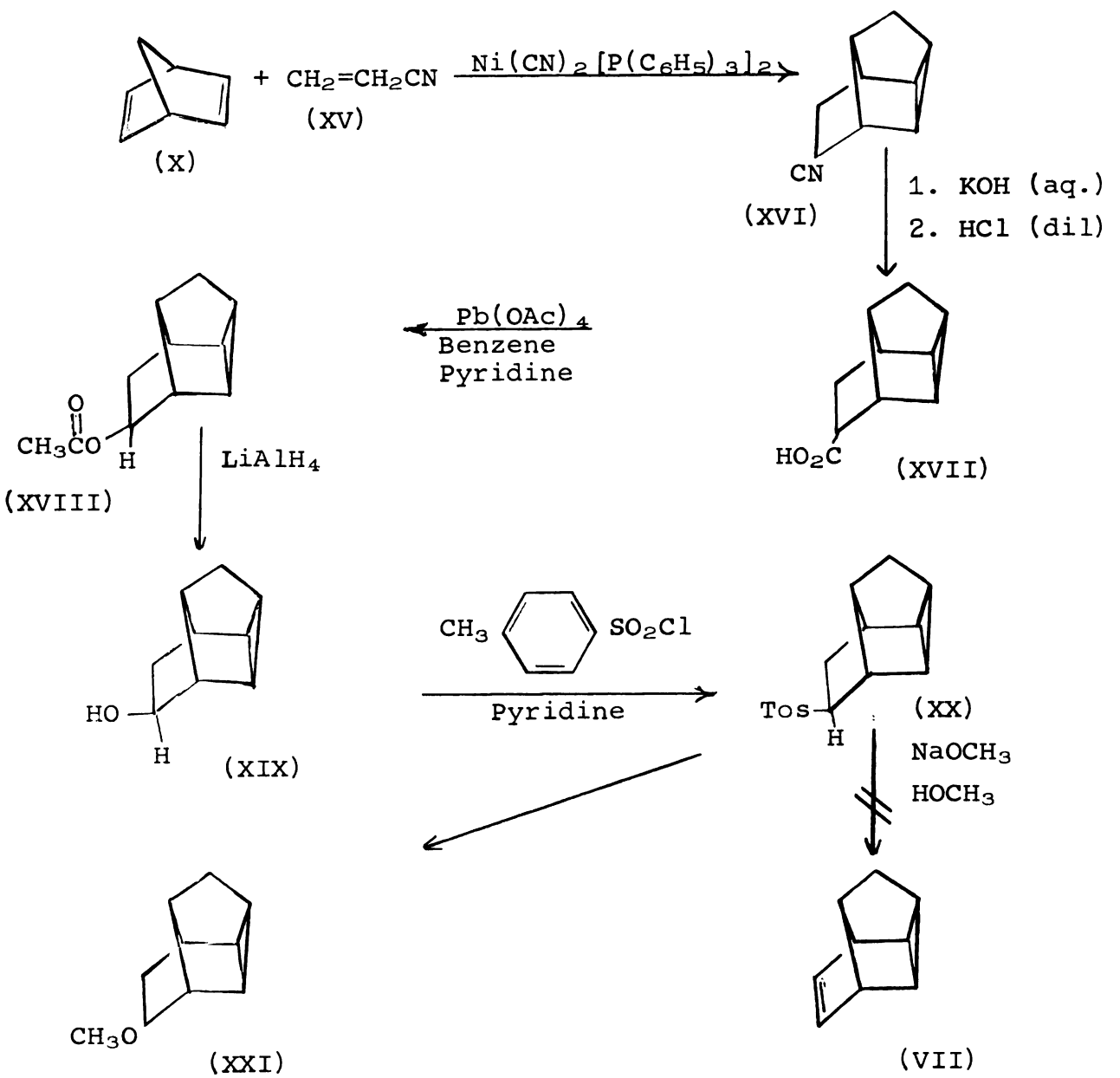
Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (VII) could not be isolated when the saturated cis-endo-diacid XIII was treated with lead tetraacetate. Instead, a compound giving strong bands in the carbonyl region of the infrared was obtained. This suggested an acetate or a lactone; however, the product was not further investigated.

The second route to VII involved the elimination of p-toluene sulfonic acid from tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-tosylate (XX). The series of reactions involved in the preparation of the tosylate are given in Scheme II.

8-Cyanotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (XVI) was obtained by heating norbornadiene(X) and acrylonitrile(XV) in the presence of dicyanobis(triphenylphosphine)nickel(II) in a sealed tube (12). Hydrolysis of the nitrile XVI with aqueous sodium hydroxide followed by acidification with dilute hydrochloric acid gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-carboxylic acid (XVIII). Treatment of the acid XVIII with lead tetraacetate in the presence of pyridine gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate (XVIII) (13,14).

From the work of E. J. Corey and J. Casanova (15), involving the mechanism of the decarboxylation (Figure 1), it is apparent that the exo-acetate would be expected.

SCHEME II


+ $CH_2=CH_2CN$
(XV)
$Ni(CN)_2[P(C_6H_5)_3]_2$
(X)
CN
(XVI)
1. KOH (aq.)
2. HCl (dil)
HO_2C
(XVII)
$Pb(OAc)_4$
Benzene
Pyridine
CH_3CO
O
H
(XVIII)
$LiAlH_4$
HO
H
(XIX)
CH_3
SO_2Cl
Pyridine
Tos
H
(XX)
$NaOCH_3$
$HOCH_3$
CH_3O
(XXI)
(VII)

After generation of the carbonium ion, attack of the lead triacetate ion would be expected from the least hindered, exo, side of the molecule. In support of this both endo- and exo-norbornane-2-carboxylic acid formed exo-norbornane-2-acetate upon decarboxylation with lead tetraacetate.

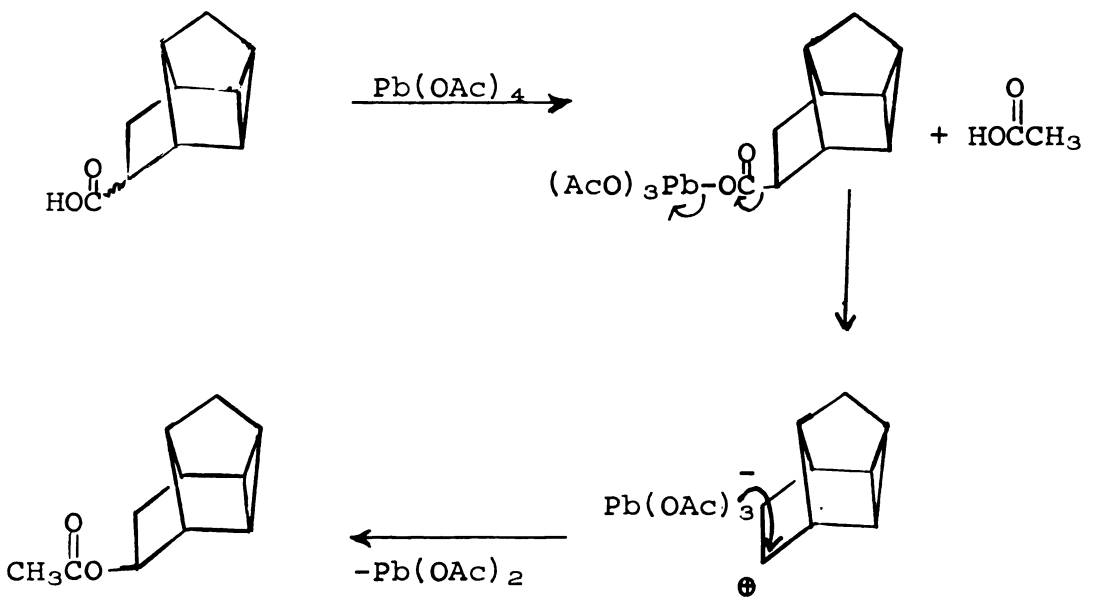


Figure 1. Mechanism of the conversion of tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nona-8-carboxylic acid to tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-acetate by reaction with lead tetraacetate.

Reduction of the acetate XVIII with lithium aluminum hydride gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-ol (XIX) (14). The infrared spectrum of the alcohol XIX showed no absorption in the carbonyl region, but did have a strong broad band at 3310 cm^{-1}, which is characteristic of (O-H) stretching. Elemental analysis and n.m.r. confirmed the structure. The alcohol XIX is believed to be the exo alcohol since reduction of esters occur with retention of configuration (16).

Finally, treatment of the alcohol XIX with p-toluene sulfonyl chloride in the presence of pyridine gave tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-tosylate (XX). An infrared spectrum indicated the absence of (O-H) stretching and the presence of R-SO_2-Ar absorptions at 1355 and 1170 cm^{-1}. Also, vapor phase chromotography showed only a trace of material with a retention time corresponding to the alcohol XIX.

Upon treatment of the tosylate XX with sodium methoxide in refluxing methanol, no reaction could be detected after 24 hours by v.p.c. After 48 hours a small peak with a retention time close to that of the alcohol XIX was observed. This was assigned to the methyl ether XXI.

The lack of reactivity of the tosylate XX in the presence of strong base suggests that the attack of the methoxide ion may be sterically hindered. This is reasonable since the exo-alcohol XIX would lead to the exo-tosylate XX which should require the elimination of an endo proton at carbon atom 9 (Figure 2).

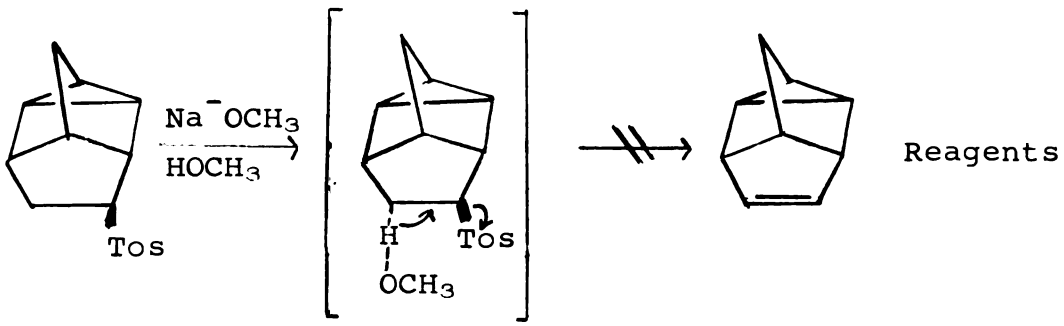


Figure 2. Mechanism of tosylate eliminations in the formation of alkenes.

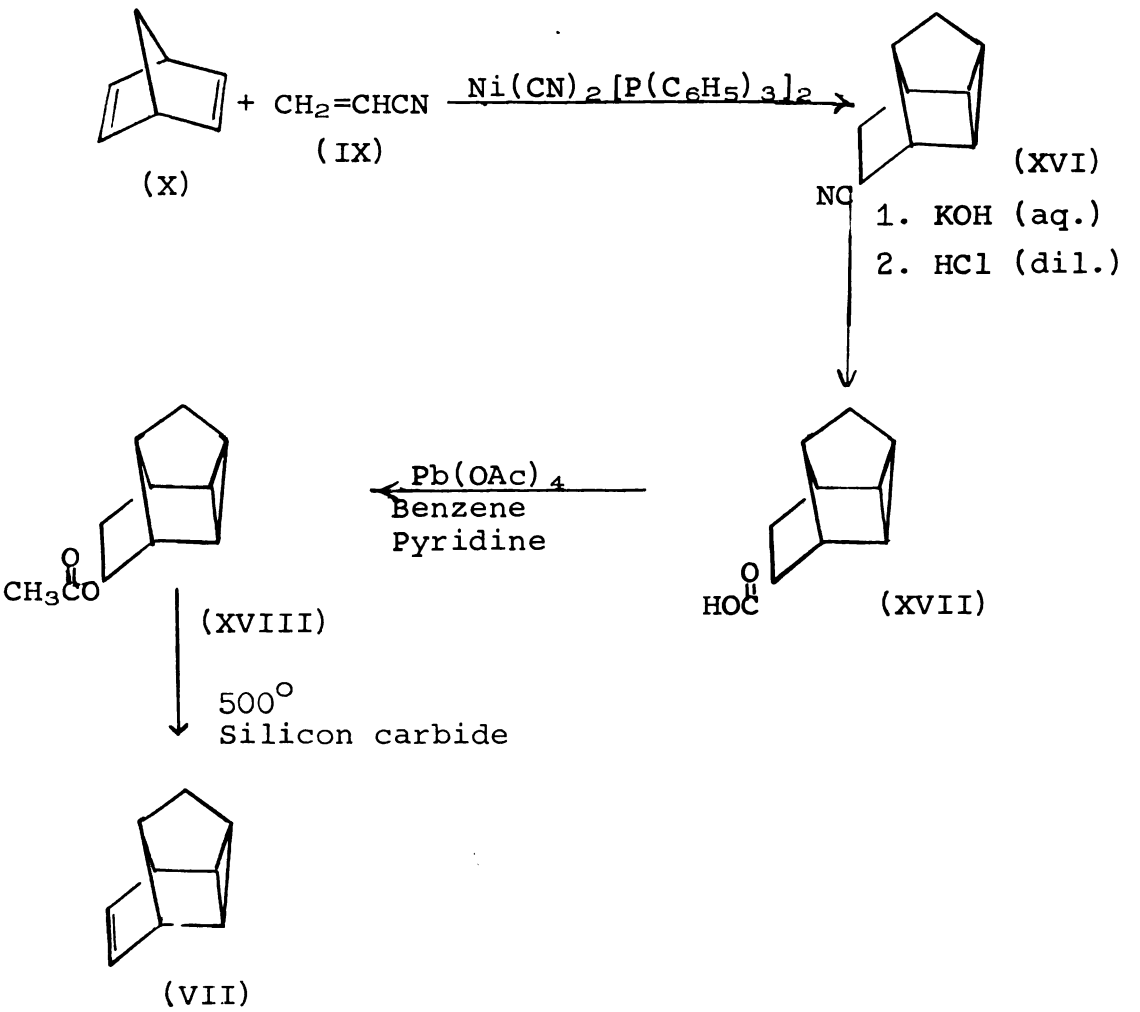
The construction of a model readily demonstrates that a considerable amount of steric hinderance must be overcome to abstract the endo proton. It is believed that the tosylate elimination is ineffective for this reason.

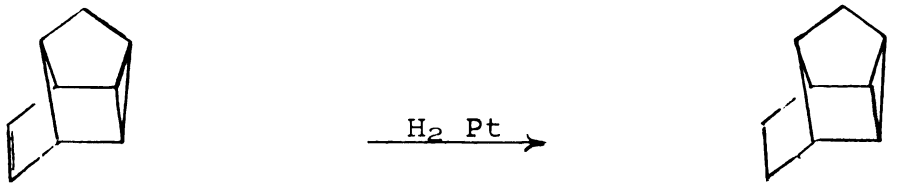
The reaction sequence which finally led to tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene is given in Scheme III.

Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate (XVIII) was prepared as previously described. With nitrogen as the carrier gas, the acetate XVIII was passed through a tube packed with granular silicon carbide and heated to 500°. The crude alkene VII was distilled at atmospheric pressure under nitrogen, bp 147° (740 mm.). Carbon hydrogen analysis and mass spectroscopy data agreed with the structure and molecular weight of the compound. The infrared spectrum showed absorptions at 1565 and 799 cm^{-1} characteristic of (C=C) stretching and the nortricyclene structure, respectively. The n.m.r. spectrum gave a triplet at τ 4.2 (2 H) which lies in the region characteristic of olefinic protons and a doublet at τ 8.79 (2 H, relative area 1.4:1) indicative of cyclopropyl protons.

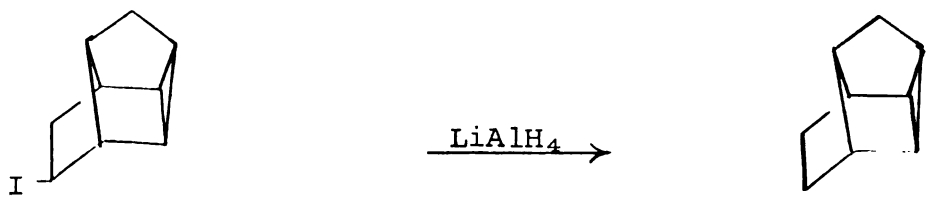
Catalytic reduction of VII with Adams' catalyst required one mole of hydrogen per mole of alkene. The product, tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (XXII), gave an infrared spectrum corresponding to a sample of XXII which had been prepared by the reduction of 8-iodotetracyclo[4.3.0,0.^{2,4}0.^{3,7}]-nonane (XXIII) by R. LaCount (17).

SCHEME III


+ CH2=CHCN
(IX)
(X)
Ni(CN)2[P(C6H5)3]2
(XVI)
NC
1. KOH (aq.)
2. HCl (dil.)
Pb(OAc)4
Benzene
Pyridine
HOC
O
(XVII)
CH3CO
O
(XVIII)
500°
Silicon carbide
(VII)



(VII) (XXII)



(XXIII) (XXII)

The n.m.r. spectrum of the olefinic protons proved quite interesting (Figure 3). The observed spectrum was a triplet (2H), relative area 1.3:1.9:1). This spectrum did not, at first, appear to correspond to the spectrum predicted for these protons. It was believed that the olefinic protons would appear as two doublets; the coupling between protons H_a and H_b being large while the coupling between H_a and H_c would be small (Figure 6).

Investigation of the n.m.r. spectra of norbornene (XXIV) and of norbornadiene(X) proved particularly useful since the norbornane skeleton is found in the tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]-nona-8-ene molecule. This skeleton corresponds to atoms 1,2, 3,6,7,8, and 9 of the alkene VII. In all three compounds the olefinic protons are in nearly the same environment.

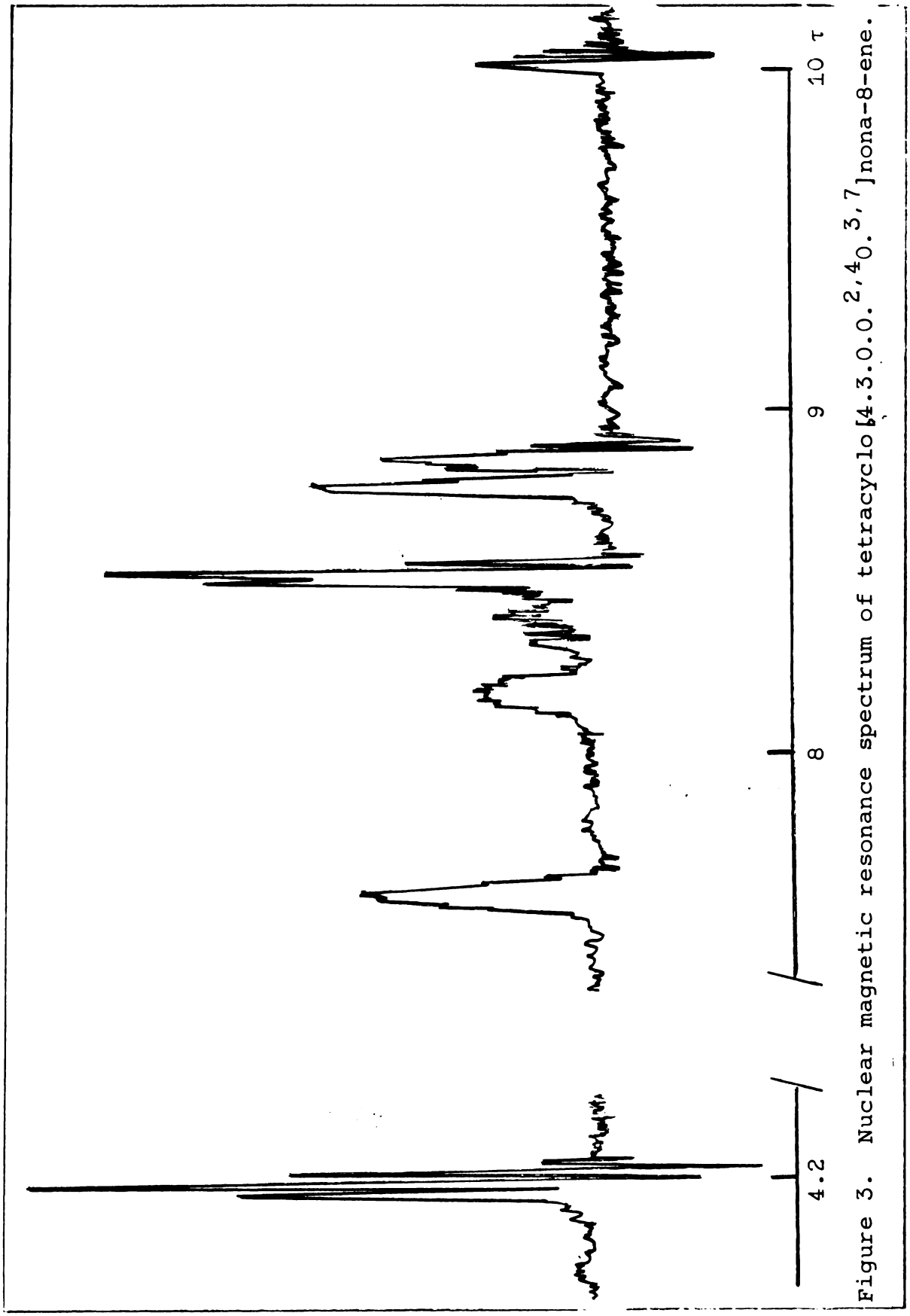


Figure 3. Nuclear magnetic resonance spectrum of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene.

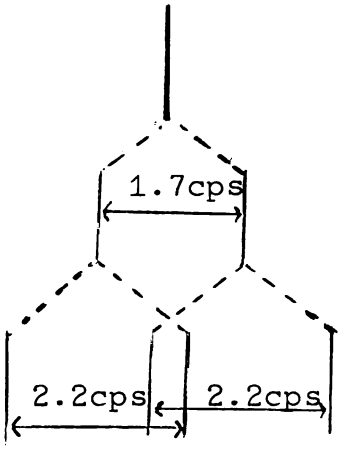
Norbornadiene is an AA'BB' system in which the coupling between H_a and H_b and between H_a and H_c gives rise to two doublets (relative areas: 1.3:1.2:1:1.3, J_{ab} 2.2 cps and J_{ac} 1.7 cps, Figure 4).

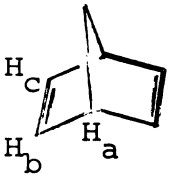
The spectrum of norbornene like that of the alkene VII consists of a triplet in the olefinic region (relative area: 1:1.8:1, J_{ab} 1.7 cps, J_{ac} = 1.8 cps (Figure 5)).

It follows from norbornadiene(X) that the triplets in both norbornene(XXIV) and tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene(VII) consists of two overlapping doublets (J_{ab} = J_{ac} = 1.7 cps, Figure 6).

The fact that proton H_a couples with proton H_b as strongly as proton H_c suggests that there may be something peculiar about the geometry of the molecule. By building a model it becomes evident that the carbon-hydrogen bonds at H_a, H_b and H_c are nearly coplaner as in norborene and norbornadiene. The coupling constant between H_a and H_c, J_{ac} = 1.7 cps, is consistent with reported allylic coupling constants (18).

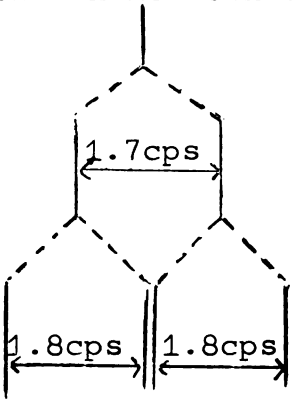
The coupling constant between H_a and H_b is expected to be approximately 2.1 cps as reported for cyclopentene (19). Since the cyclopentene ring of VII is strained, the angle (Q) between H_a and H_b would be larger than that of cyclopentene itself (Figure 7).

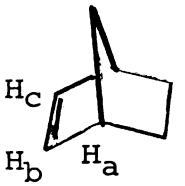




(X)

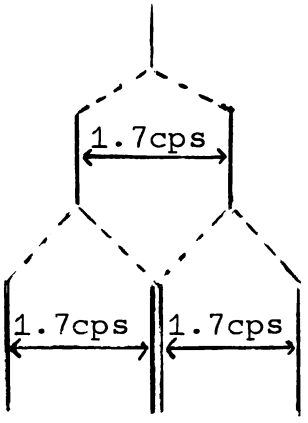
Figure 4. Diagram of the coupling constants of the nuclear magnetic resonance spectrum of the olefinic protons in norbornadiene.

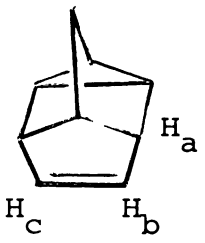




(XXIV)

Figure 5. Diagram of the nuclear magnetic resonance coupling constants of the olefinic protons in norbornene.





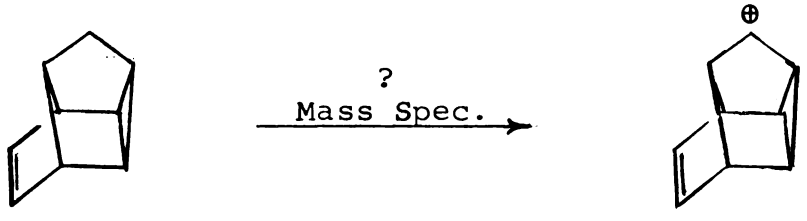
(VII)

Figure 6. Diagram of the nuclear magnetic resonance coupling constants of the olefinic protons in tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene.

Figure 7. Angle dependence of nuclear magnetic resonance coupling constance in cyclopentene and cyclobutene.

As the angle is increased it would approach that of cyclobutene (Q'). The coupling between H_d and H_e has been reported to be 1.5 cps. The value of 1.7 cps is, therefore, reasonably accounted for by an increase in the angle (Q). As the angle opens it approaches that of cyclobutene.

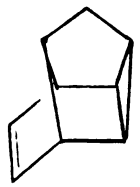
The mass spectrum of the alkene VII also proved to be interesting. The parent peak, as expected, had a mass of 118. The n-1 peak, however, was even more intense than the parent peak. This indicates that a rather stable species with a mass of 117 has been formed. One possibility is that one of the protons on carbon 5 has been cleaved to form the carbonium ion II. If this is the case the prospects for producing the ion chemically are encouraging.



(VII) (II)

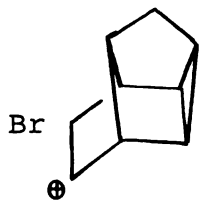
The structure of alkene VII suggests that the compound may have interesting chemical properties. The presence of a cyclopropane ring in a position which is homoallylic to

the double bond presents the possibility of addition reactions occurring with rearrangement. The synthesis of 5-bromotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene may be postulated if a bromonium ion adds to the alkene VII to form a carbonium ion which rearranges (XXV, XXVI) and finally eliminates hydrogen bromide.

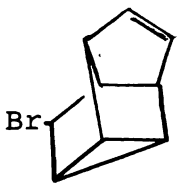


(VII)

Br_2

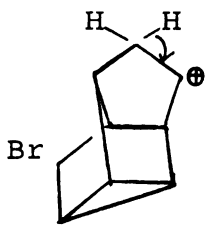


(XXV)



(XXVII)

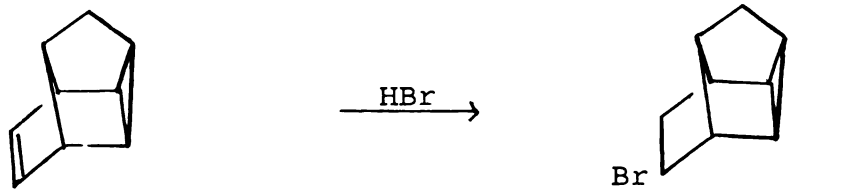
-HBr



(XXVI)

Direct bromination of the alkene in carbon tetrachloride at 45^{o} resulted in a mixture which appeared to be composed of three major components when analyzed by v.p.c. The three were in a ratio of 1:1:1 with retention times of 1, 3 and 14 minutes, respectively. The first peak was starting material; the second, upon close examination, proved to be two components nearly superimposed and the last, was a broad peak suggesting the possibility of more than one compound.

The ratio of vinylic protons to the two equivalent cyclopropyl protons of the second component was 1:2, rather than 1:1, as expected for the brominated alkene. This suggested that eliminated hydrogen bromide reacted with the starting alkene VII to form the 8-bromotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane(XXVIII).

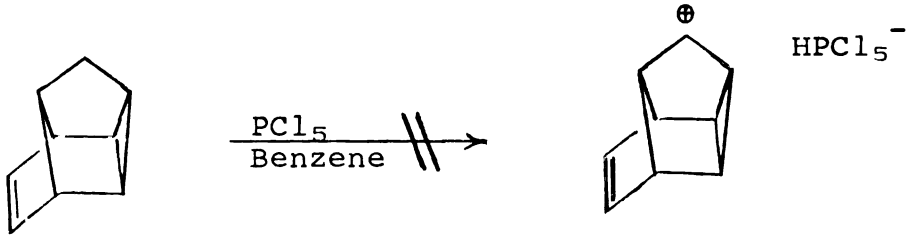


(VII) (XXVIII)

The component with a retention time of 14 minutes was assigned to dibromoderivatives. Isolation of each compound in the second component of the v.p.c. was foregone in hopes of finding a more favorable method of bromination.

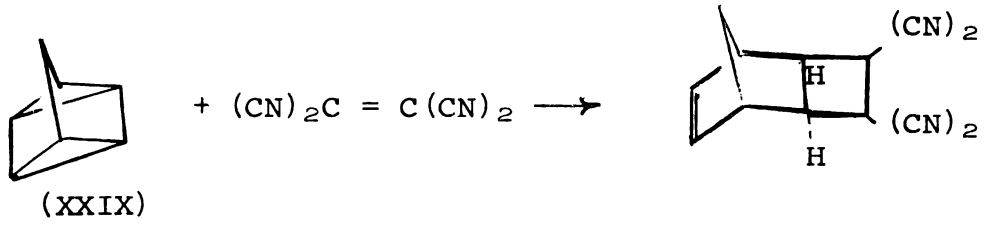
Bromination with pyridine perbromide appeared to be the reagent of choice since hydrogen bromide would be removed by the reaction media as pyridinium bromide. The reaction of equal molar quantities of the alkene VII and pyridine perbromide in CCl_4 for two hours at 90^{o} gave 20% starting material and 80% of a material assigned to dibromoderivatives. No component with a retention time similar to that expected for the 5-bromoalkene(XXVII) could be found with the v.p.c.

The possibility of hydride abstraction with the formation of a salt was also investigated.

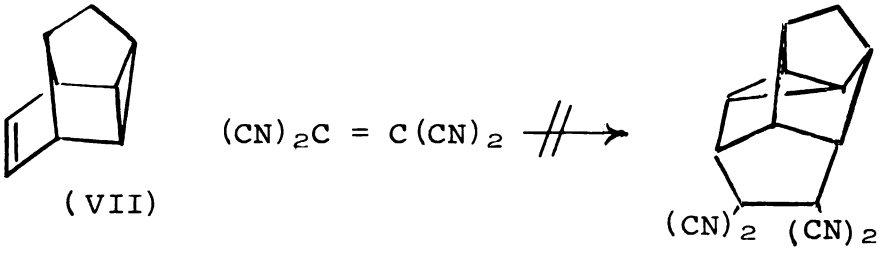


Treatment of the alkene VII with phosphorous pentachloride in both carbon disulfide and nitromethane at Dry Ice-acetone temperatures led to extensive decomposition. No identifiable product could be isolated.

A pseudo Diels-Alder reaction of tetracyclo[4.3.0.0.^{2,4} 0.^{3,7}]nona-8-ene with tetracyanoethylene was suggested by the 1,2 addition of tetracyanoethylene to quadricyclane (XXIX) (21). Refluxing the alkene(VII) with tetracyanoethylene in methylene chloride, benzene and xylene all led to recovery of the tetracyanoethylene.



(XXIX)



(VII)

EXPERIMENTAL

A. General Procedures and Apparatus

The infrared spectra were obtained on a Perkin-Elmer 237B Grating Infrared Spectrophotometer. The sample holders in all cases were either sodium chloride cells or sodium chloride plates. Nuclear magnetic resonance spectra were recorded on a Varian A-60 high resolution spectrometer using tetramethylsilane as an internal reference. Vapor phase chromatography was done on an Areograph model A-90-P3 Gas Chromatograph.

Melting points were determined on a Thomas Hoover capillary melting point apparatus.

Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

B. Dimethyl tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene-dicarboxylate(XI)

Freshly distilled norbornadiene (12.9 gm., 0.14 mole) and dimethyl acetylenedicarboxylate (19.9 gm., 0.14 mole) were heated together at 105° for 20 hours under a nitrogen atmosphere. Vacuum distillation of the reaction mixture yielded 33 gm. (0.10 mole) 70%, of the diacid, bp 95-100° (0.18 mm.). The distillate crystallized almost immediately. Recrystallization from pentane produced large white crystals, mp 64-65° (lit. (12) 64°).

C. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene-8,9-dicarboxylic acid(XII)

To 85 ml. of a stirred solution of 1.1 M potassium hydroxide was added 11 gm. (0.045 mole) of 8,9-dicarbomethoxy-tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene(XI). The heterogeneous mixture was refluxed for three hours under nitrogen. The solution was cooled to room temperature and was extracted with diethyl ether. The aqueous layer was treated with dilute hydrochloric acid until precipitation was complete. The product was isolated by filtration. The unsaturated diacid XII was obtained as a white crystalline solid (9.0 gm., 0.044 mole) 96%, mp 217-218°, $\nu_{max.}^{CHCl_3}$ 2980, 1720, 1580 and 1270 cm^{-1}.

D. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-endo-dicarboxylic acid(XIII)

Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-endo-dicarboxylic acid (9.7 gm., 0.046 mole) was dissolved in 30 ml. of benzene and 10 ml. of pyridine. The solution was placed in the bomb of a Parr hydrogenation apparatus along with 60 mg. of Adams' catalyst, platinum oxide. The initial pressure was 15.5 lb./in.^{2} and after 12 hours the pressure dropped to 12.0 lb./in.^{2}. The tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]-nonane-8,9-dicarboxylic acid(XIII) precipitated as a white solid. The platinum was removed by dissolving the diacid (XIII) in tetrahydrofuran followed by filtration. After removal of the solvent (rotoevaporator), the diacid (9.7 gm., 0.046 mole) 100%, was obtained as a white powder, mp 206-207°, $\nu_{max.}^{CHCl_3}$ 3460(broad), 3020, 1690, and 1198 cm^{-1}.

E. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-endo-dicarboxylic acid anhydride(XIV)

Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8,9-dicarboxylic acid (XIII), (0.5490 gm., 2.67 x 10^{-3} mole) was placed in a small vial which in turn was placed in a 125 ml. side arm flask. The flask was evacuated (aspirator), closed and heated to 220° by submersion in a preheated oil bath. After the evolution of gas appeared complete, the flask was swept out with nitrogen. No precipitate was observed as the gas was passed through a barium hydroxide solution. The isolated compound

(0.4955 gm., 2.6 x 10^{-3} mole) showed a loss of weight corresponding to the elimination of one mole of water per mole of diacid. A white crystalline solid XIV was obtained by recrystallization from cyclohexane, mp 118-120° (lit. (11) 120°), $\nu_{max.}^{CHCl_3}$ 3000, 1850, 1770, 1200, 1075, 955, and 915 cm^{-1}.

F. 8-Cyanotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (XVI) (12)

Freshly distilled norbornadiene (24 gm., 0.27 mole) and freshly distilled acrylonitrile (16 gm., 0.30 mole) were placed in a heavy walled tube (60 ml. capacity). To this 0.5 gm (7.4 x 10^{-4} mole) of finely powdered dicyanobis(triphenylphosphine)nickel(II) were added. Dissolved oxygen was removed by passing dry nitrogen through the solution (5 min.). The tube was sealed after being cooled in a Dry Ice-acetone bath.

The sealed tube was then immersed in an oil bath preheated to 120°. It was shaken every 15 to 20 minutes during the first four hours to prevent the nickel catalyst from caking. After 18 hours the tube was allowed to cool to room temperature and then opened. The catalyst was removed by filtration and unreacted starting materials were distilled from the solution at atmospheric pressure. Vacuum distillation yielded 18.5 gm. (0.13 mole) 47.5%, bp 57° (0.10 mm) of XVI.

G. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-carboxylic acid (XVII)

To a solution containing 40 gm. (0.71 mole) of potassium hydroxide in 100 ml. of water, was added 21.10 gm. (0.145 mole) of 8-cyanotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (XVI). The heterogeneous solution was refluxed for 12 hours under nitrogen. Acidification with dilute hydrochloric acid gave an oil which was easily separated from the aqueous layer (extraction with ether led to unworkable emulsions). The acid was obtained in crystalline form after seeding and prolonged standing. The hydrolysis yielded 22.4 gm. (0.136 mole) 94%, of the white, unpleasant smelling, tetracyclo-[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-carboxylic acid(XVII), mp 57-58.5°, $\nu_{max.}^{CHCl_3}$ 3000(broad), 1690, 1410, and 1280 cm^{-1}.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.38; mol. wt. 164; Found: C, 72.05, H, 7.22.

H. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate(XVIII) (14)

Into a two-liter, three-necked flask fitted with a reflux condenser, mechanical stirrer and a dropping funnel, was placed 140 gm. (0.37 mole) of lead tetraacetate, 450 ml. of benzene and 30 ml. of pyridine. After flushing the vessel with nitrogen, the benzene-lead tetraacetate mixture was brought to reflux with stirring. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]-nonane-8-carboxylic acid(XVII), (47 gm., 0.28 mole) dissolved in 50 ml. of benzene was added dropwise over a period of one

hour. The mixture was refluxed for an additional hour before cooling and filtration. The filtrate was washed four times with dilute hydrochloric acid, once with a dilute potassium carbonate solution and once with water. Vacuum distillation after drying over magnesium sulfate gave 28.6 gm. (0.16 mole) of the acetate XVIII, 56.2%, bp 56-60° (0.15 mm), $\nu_{max.}^{NaCl}$ 3045, 2925, 2850, 1730, 1240, 1025, and 800 cm^{-1}(neat); nmr: τ 8.0 (multiplet, 5 H), τ 8.15 (sharp singlet, 3 H), τ 8.5 (broad singlet, 3 H), τ 8.7 (doublet, J = 4 cps, 1 H), and τ 9.22 (doublet, J = 5 cps, 2 H).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.88; mol. wt. 178; Found: C, 74.79; H, 7.88.

I. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-ol(XIX) (14)

Into a flask fitted with a reflux condenser was introduced 150 ml. of dry tetrahydrofuran and 2.4 gm. (6.34×10^{-2} mole) of lithium aluminum hydride. To this solution 8 gm. (4.5×10^{-2} mole) of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate(XVIII) dissolved in 10 ml. of tetrahydrofuran was added dropwise.

After refluxing for 18 hours, the excess lithium aluminum hydride was destroyed by the dropwise addition of ethyl acetate. The reaction mixture was then treated with 20 ml. of sodium hydroxide (8 gm./20 ml.). The gummy precipitate which formed was removed by filtration. The sodium hydroxide solution

being partially insoluble in the tetrahydrofuran was removed. The alcohol XIX was taken up in ether and dried over magnesium sulfate. The tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-ol(XIX), (4.5 gm., 0.033 mole) 73%, was isolated by distillation under reduced pressure, bp 103-106^{o} (aspirator), $\nu_{max.}^{NaCl}$ 3310(broad), 3030, 2920, 2840, 1070, 1035, 990 and 799 cm^{-1}(neat); nmr: τ 5.16 (singlet, 1 H), τ 5.94 (quartet, J = 7 cps, J = 2 cps, 1 H), τ 8.02 (broad singlet, 4 H), τ 8.45 (singlet, 3 H), τ 8.93 (multiplet, 1 H), and τ 9.24 (doublet, J = 5 cps, 2 H).

Anal. Calcd. for $C_9H_{12}O$: C, 79.36; H, 8.90; mol. wt. 136; Found: C, 79.03; H, 8.91.

J. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-tosylate(XX)

Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane-8-ol(XIX), (4.5 gm., 0.033 mole) was dissolved in 12 ml. of pyridine and cooled to 0^{o}. To the stirred alcohol solution was added 12 ml. of pyridine containing 8.3 gm. (0.043 mole) of p-toluene sulfonyl chloride over a period of one-half hour. The temperature was then raised to 60^{o} for an additional hour. After cooling to room temperature, the solution was poured into 100 ml. of ice-cold dilute hydrochloric acid. The oil which formed was taken up in ether, then washed three times with cold dilute hydrochloric acid and once with cold water. The solution was dried over anhydrous magnesium sulfate and finally the ether was removed (rotoevaporator) leaving 9.1 gm. (0.031 mole)

of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-tosylate, 95%, $\nu_{max.}^{NaCl}$ 3040, 2925, 2850, 1690, 1355, 1170, 880, 802 cm^{-1} (neat).

K. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene(XII)

A Pyrex tube 1.5 cm. in diameter packed with 28 cm. of granular silicon carbide (10 mesh) eas placed vertically in a tube furnace. The temperature was raised to 500° (chromel-aluminel thermocouple with direct reading potentiometer) and the flow rate of cry nitrogen was adjusted to two bubbles per second. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonyl-8-acetate (XVIII), (23.0 gm., 0.128 mole) was dropped on the column at a rate of 12 to 15 drops per minute. The product was collected in a 50 ml., three-necked flask fitted with a reflux condenser and submerged in a Dry Ice-acetone bath.

The light brown solid was taken up in ether and washed three times with a dilute potassium carbonate solution followed by a final wash with water. After drying with anhydrous magnesium sulfate, the alkene was isolated by distillation under nitrogen at atmospheric pressure. The alkene VII, (8.2 gm., 0.069 mole) 54%, was obtained as a pale yellow liquid, bp 145-147° (740 mm), $\nu_{max.}^{NaCl}$ 3050, 2950, 1320, 1265, 925, 799, 775, and 700 cm^{-1} (neat); nmr: τ 4.2 (triplet, J = 1.7 cps, 2 H), τ 7.55 (singlet, 2 H), τ 8.15 (broad singlet, 1 H), τ 8.46 (multiplet, 3 H), and τ 8.80 (doublet, J = 9 cps, 2 H).

Anal. Calcd. for C_9H_{10}: C, 91.53; H, 8.47; mol. wt. 118. Found: C, 91.78; H, 8.34.

L. Dicyanobis(triphenylphosphine)nickel(II) (12)

Triphenylphosphine (78 gm., 0.30 mole) and nickel(II) cyanide tetrahydrate (11.0 gm., 0.06 mole, vacuum dried at 100°) were refluxed in absolute ethanol for 48 hours. The crude product was isolated by decanting the supernatant. The yellow solid was washed three times with ethanol and then taken up in methylene chloride. Upon removal of the methylene chloride (rotoevaporator), 15.2 gm. (0.024 mole) 40% of a light yellow powder, dicyanobis(triphenylphosphine) nickel(II), was isolated.

M. 8,8,9,9-Tetracyanotetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane (20)

Norbornadiene (0.72 gm., 7.8×10^{-3} mole) was added to a cold solution of tetracyanoethylene (1.0 gm., 7.8×10^{-3} mole) in 25 ml. of benzene. The solution immediately turned red. After refluxing for one-half hour, the product crystallized out as a brown powder. The yield was essentially quantitative (1.7 gm., 7.7×10^{-3} mole). Recrystallization from benzene gave a white crystalline material, mp 187-189° (lit. (20) 186-188°).

N. Tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nonane

The reduction of tetracyclo[4.3.0.0.^{2,4}0.^{3,7}]nona-8-ene (VII) was carried out under atmospheric pressure in a micro hydrogenation apparatus with a 100-ml. hydrogen reservoir. Approximately 40 mg. of Adams' catalyst, reduced platinum oxide, was reduced to free platinum in 10 ml. of methanol prior to the introduction of the alkene(VII). The alkene (0.4 gm., 3.4 x 10^{-3} mole) dissolved in 5 ml. of methanol was introduced into the reaction vessel with a hypodermic syringe through a rubber septum cap. The uptake of hydrogen stopped after 75.1 ml. (67.0 ml. at S.T.P.; 3.0 x 10^{-3} mole; 88.4%) had been used. Isolation by distillation proved unsuccessful because the alkane codistilled with the methanol. The alkane was finally isolated by preparative v.p.c. on an SE-30 column at 94^{o}. (He = 40 lb./in.^{2}) $\nu_{max.}^{NaCl}$ 3040, 2930, 2860, 1310 and 790 cm^{-1} (neat). The retention time and infrared spectrum corresponded to a sample of the alkane prepared by R. LaCount (16).

LITERATURE CITED

1. W. v. E. Doering and W. R. Roth, Angew. Chem. Int. Ed., 2, 115 (1963).

2. G. Schröder, Angew. Chem. 722 (1963), Int. Ed., 2, 481 (1963).

3. J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73 2509, 3542 (1951).

4. H. C. Brown and M. Bell, J. Am. Chem. Soc., 85, 2324 (1963).

5. S. Winstein et al., J. Am. Chem. Soc., 77, 4183 (1955); 78, 592 (1956); 85, 2324 (1963); 88, 3133 (1966).

6. E. van Tamelen and S. Pappus, J. Am. Chem. Soc., 85, 3297 (1963).

7. C. A. Grob, M. Ohta, E. Renk and A. Weiss, Helv. Chim. Acta., 41, 1191 (1958).

8. C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem. 70, 343 (1958).

9. C. H. Snyder and A. R. Soto, J. Org. Chem., 29, 742 (1964).

10. D. Froemsdorf, C. Collins, G. Hammond and C. DePuy, J. Am. Chem. Soc., 81, 643 (1959).

11. R. C. Cookson, J. Dance, and J. Hudec, J. Chem. Soc., 5416 (1964).

12. G. N. Schrauzer and P. Glockner, Ber., 97, 2451 (1964).

13. L. Birladeanu, T. Hanafusa, and S. Winstein, J. Am. Chem. Soc., 88, 2315 (1966).

14. P. K. Freeman, D. M. Balls, Abstract of Papers, Am. Chem. Soc. Meeting, Organic Paper No. 39, Sept. 1966.

15. E. J. Corey and J. Casanova, J. Am. Chem. Soc., 85, 165 (1963).

16. H. C. Brown and A. Trukamoto, J. Am. Chem. Soc., 81, 502 (1959); 86, 1089 (1964).

17. R. LaCount and E. LeGoff, Private Communication.

18. R. M. Silverstein and C. Bassler, Spectrometric Identification of Organic Compound, John Wiley and Sons Inc., New York, 1963.

19. G. V. Smith and H. Kriloff, J. Am. Chem. Soc., 85, 2016 (1963).

20. A. T. Bloomquist and Y. C. Meinwald, J. Am. Chem. Soc., 81, 667 (1959).

21. C. D. Smith, J. Am. Chem. Soc., 88, 4274 (1966).