


AN ABSTRACT OF THE THESIS OF

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Title SYNTHESIS OF SOME BICYCLO[6.1.0]NONANE

DERIVATIVES

Abstract approved 

Bicyclo [6.1.0] non-4-ene was prepared by two routes; (1) reaction of cis-cis-1,5-cyclooctadiene with methylene iodide and zinc-copper couple, (2) sodium-methanol reduction of 9,9-dibromobicyclo [6.1.0] non-4-ene. The bicyclononene was characterized by its infrared spectrum, nuclear magnetic resonance spectrum and common physical properties. The olefin was hydrogenated to bicyclo [6.1.0] nonane.

9,9-Dibromobicyclo [6.1.0] non-4-ene was prepared by dibromocarbene addition to 1,5-cyclooctadiene. Structure proof was provided by the analytical results, infrared spectrum, nuclear magnetic resonance spectrum and the conversion to bicyclo [6.1.0] non-4-ene.

The acetolysis of bicyclo [6.1.0] non-4-ene was carried out and the products analyzed by vapor phase chromatography. At least eight major products were indicated.

SYNTHESIS OF SOME BICYCLO [6.1.0] -
NONANE DERIVATIVES

by

ROBERT GENE WALL

A THESIS

submitted to

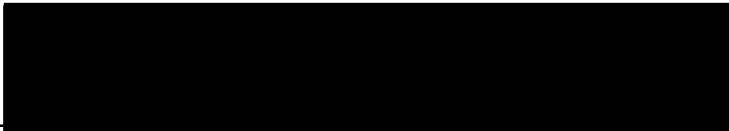
OREGON STATE UNIVERSITY

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the requirements for the
degree of


MASTER OF SCIENCE

August 1963

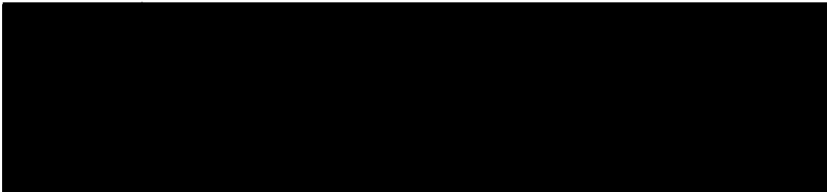
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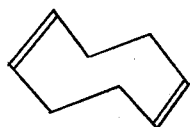
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SYNTHESIS OF SOME BICYCLO [6. 1. 0]- NONANE DERIVATIVES

INTRODUCTION

The geometric properties of medium ring carbocycles (8-12 members) have aroused considerable interest in the synthesis and study of their derivatives. Since the observation of a transannular rearrangement during the formolysis of cyclooctene oxide by Cope and co-workers (3), numerous experiments have been devised which support transannular involvement in reactions of medium ring derivatives (19 and related work; 38). Cis-cis-1,5-cyclooctadiene is a particularly interesting molecule in this respect since evidence exists that the "tub" conformation is preferred (28; 35, p. 49; 40). This allows a more intimate relationship between the double bonds than would be the case for the "chair" or "skew" conformer.



"chair"



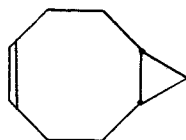
"skew"



"tub"

In fact, 1, 5-cyclooctadiene readily yields bicyclic products in highly acidic solution (9, p. 1644; 11, p. 4299).

With this prior knowledge it became of interest to synthesize bicyclo [6.1.0] non-4-ene (III). This compound has a double bond across the ring from a cyclopropyl group.



III

From the known capacity of the cyclopropyl ring for becoming involved with carbonium ion centers and for rearranging under SN1 conditions (18, p. 4850; 26; 27; 49; 50; 51; 52), the solvolysis of the bicyclononene is of interest.

The approach necessitated finding a convenient synthetic route to bicyclo [6.1.0] non-4-ene and providing evidence for this structure from measured physical properties, comparison with known physical properties, and preparation of derivatives. It would then be convenient to take a preliminary look at the acetolysis.

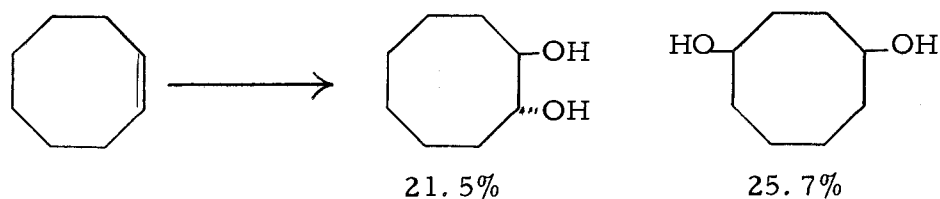
HISTORICAL

The synthesis of alicyclic derivatives of more than six ring members became of special interest only after the discovery that certain naturally occurring large ring ketones are desirable perfume ingredients (23, p. 327). The subsequent investigations made a large number of homologous alicyclics available for other studies. The inevitable comparison of the carbocycles of different ring sizes led to the surprising discovery that their physical and chemical properties varied strangely with the number of ring carbons (34, p. 42). The anomalous behavior of the medium-sized rings (8-12 members) was especially noteworthy and has resulted in considerable speculation and research activity. Scale models reveal that 8 to 12 membered rings have non-bonded eclipsed interactions in all conformations, whereas normal (5-7 members) and large rings (13 and larger) can conform to the less strained staggered conformation (34, p. 42). This predicts a unique strain feature for the 8 to 12 membered rings. Experimental verification is obtained by gas phase combustion which shows that the heat of combustion is definitely higher for the 8 to 11 membered alicyclics than for other homologs of five or more members (30, p. 271; 39, p. 1434). Thus the peculiar behavior of medium rings has been correlated with

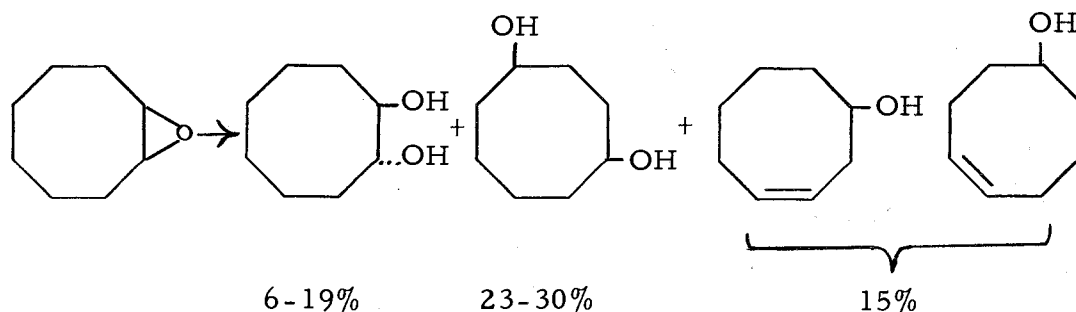
their higher energy content due to non-bonded interactions (34, p. 43; 36).

A corollary to the steric interactions in medium rings was discovered almost simultaneously by the Cope and Prelog laboratories. In 1952 both Cope (3) and Prelog (37) published evidence for "transannular effects" in certain of the medium rings. Cope continued the investigations of proximity effects in cyclooctyl derivatives while Prelog studied larger rings, in particular the cyclo-decyl series.

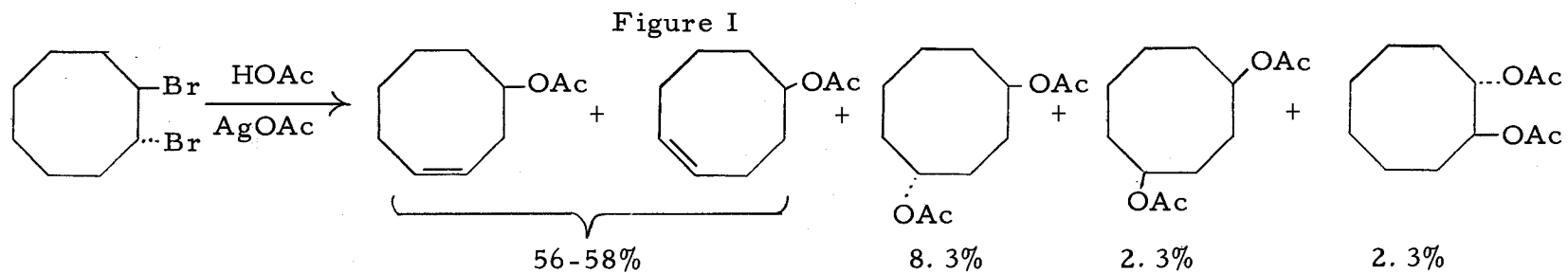
Cope and co-workers first observed a "transannular effect" in the hydroxylation of cyclooctene with performic acid. In addition to the expected trans-1,2-diol a large amount of cis-1,4-diol was produced (3, p. 5885; 7, p. 3900).



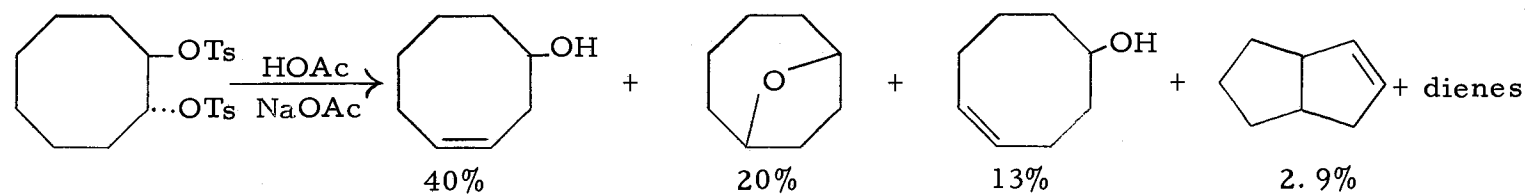
In further work the formolysis of cis-cyclooctene oxide was found to yield a mixture of diols and ene-ols (7, p. 3900).



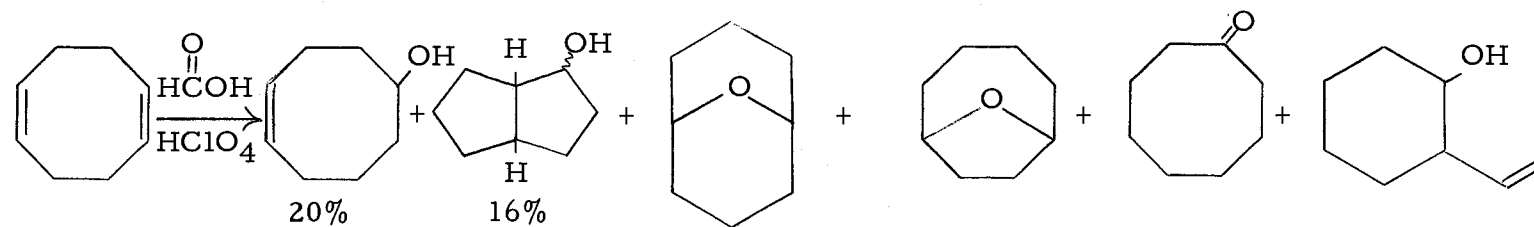
Also solvolysis of some other cyclooctyl systems gave a predominance of rearranged products. Some of those reported in 1957-59 are shown in Figure I. Solvolysis of cyclooctene oxide with different acids yields different product ratios. Specifically it was noted that stronger acids produced more transannular product (8, p.1641). Cope suggested that the driving force for the S_N1 transannular reaction is the formation of a more stable carbonium ion (12, p. 5439). In support of this, solvolysis of methylene cyclooctane oxide gives no transannular product. Opening of the epoxide gives a tertiary carbonium ion which would not be expected to rearrange to a less stable ion (12, p. 5441).



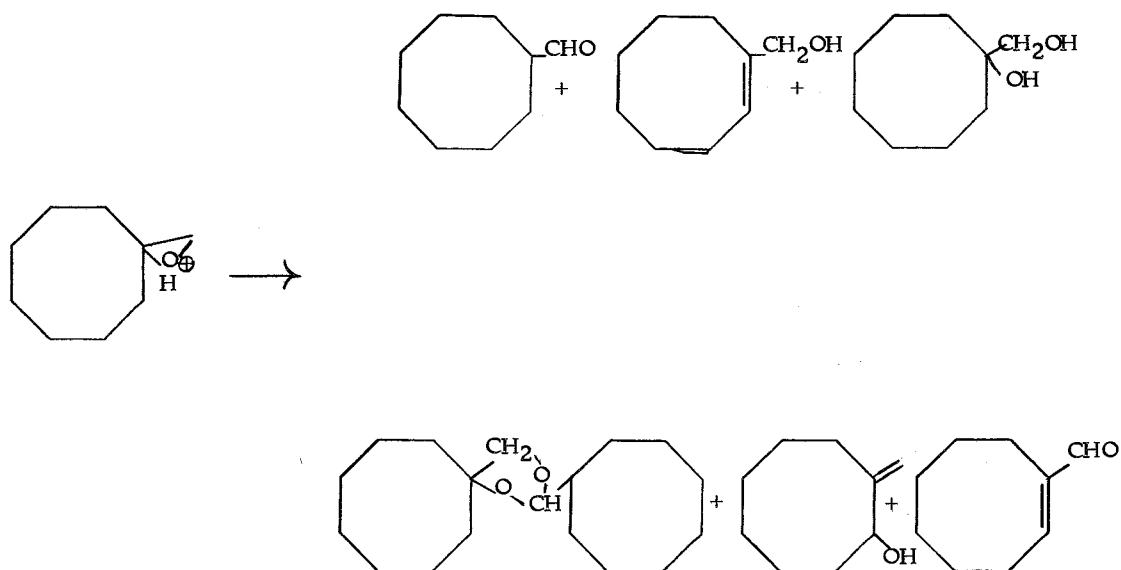
(5, p. 3886)



(10, p. 1651)

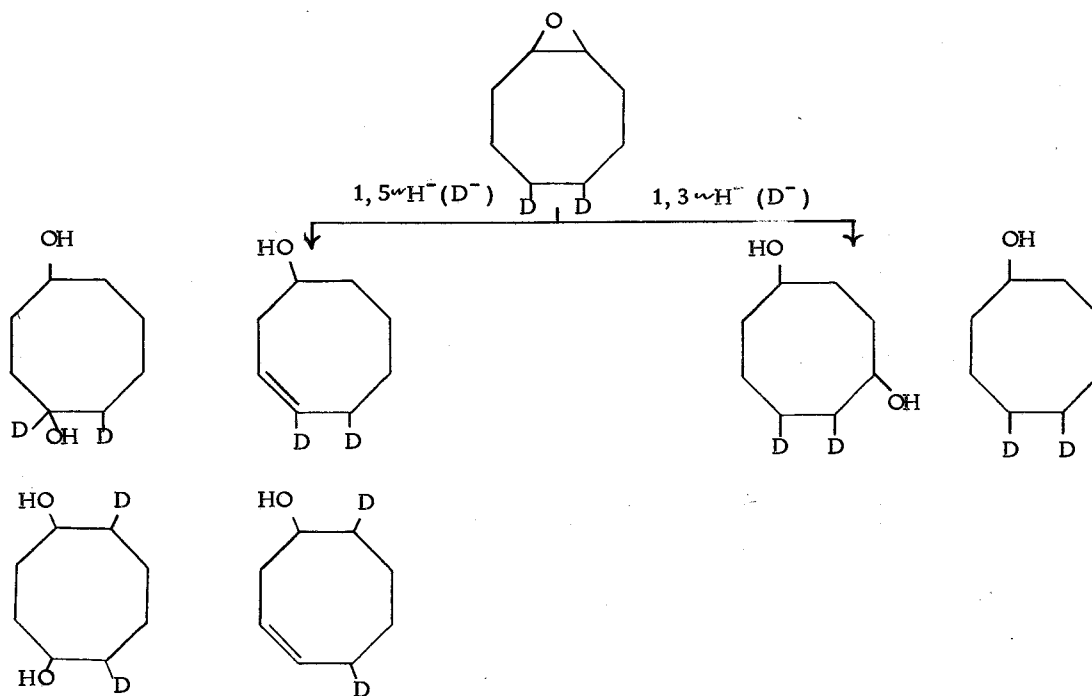


(9, p. 1643)



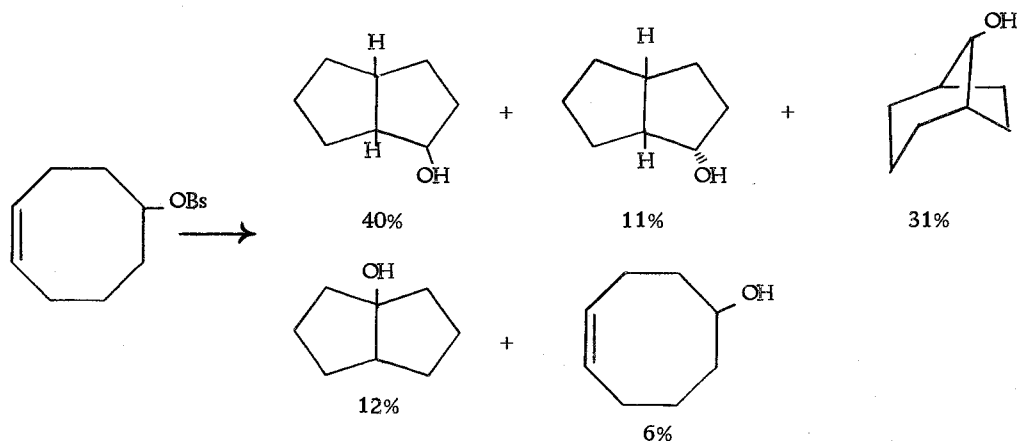
None of the identified products require a transannular reaction.

In the light of Cope's work it seems clear that the 1, 4- and 1, 5-positions of these cyclooctane derivatives are geometrically favorable for interaction. More conclusive evidence was provided in 1960 when 1, 3- and 1, 5-hydride (deuteride) shifts were detected and measured in the formolysis of 5, 6-deuterated cis-cyclooctene oxide (13, p. 6366).



Degradation studies revealed that 61% of the cis-1,4-diol and 94% of the 3-cycloocten-1-ol resulted from 1,5-hydride (deuteride) migration.

Continued investigations of the cyclooctyl system in the nineteen sixties repeatedly verified their propensity for transannular reaction (11; 18, p. 4853; 19, p. 4855; 25, p. 3160). As previously mentioned, solvolysis of 1,5-cyclooctadiene yields appreciable amounts of transannular product (9, p. 1644; 11, p. 4299). As expected, 4-cycloocten-1-yl brosylate is yet more favorable for rearrangement. Treatment with trifluoroacetic acid at 25-30° C yields the products shown below (11, p. 4299).



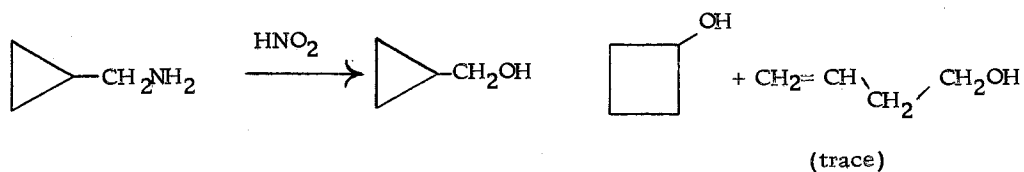
Again a majority of 1,5-interaction occurred. Formation of the carbonium ion transannular to the double bond is especially facilitated by the stability of the brosylate anion. In 1962 Cope and co-workers reported the occurrence of a 1,5-phenyl migration in the solvolysis of 5,5-diphenylcyclooctan-1-yl tosylate (19, p. 4855).

It should be mentioned that the peculiar proximity effects in eight membered rings have been shown to occur in other than solvolytic reactions. A few of these are the alumina catalyzed pyrolysis of cyclooctene oxide (21, p. 4872), pyrolysis of cyclooctyl hydrogen phthalate (16, p. 2412), and the carbenoid decomposition of diazocyclooctane (25, p. 3160). By way of contrast, the E2 reaction of trans-1,2-dibromocyclooctane with tetraethyl ammonium

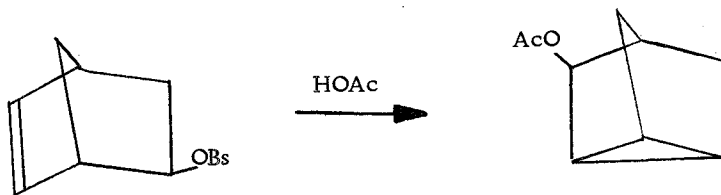
acetate gives only normal products (6, p. 3889).

From all of these studies of cyclooctyl systems it could be predicted that the generation of a reactive intermediate at a ring carbon might yield considerable transannular product. Also the presence of a functional group transannular to the reactive center would be expected to interact readily. In this respect the bicyclo-[6.1.0] non-4-ene derivatives could be significant. In this case a cyclopropyl group is transannular to a double bond. In order to understand better the importance of this arrangement one must look at the chemistry of cyclopropyl derivatives.

At least since 1917 cyclopropyl has been considered as an analog of a double bond (33, p. 1409). When conjugated with a double bond there is appreciable absorption near 2500 Å, whereas an isolated double bond generally has very little absorption in this region (31, p. 89). Other spectroscopic evidence was acquired during the nineteen forties and fifties supporting an unsaturated behavior in cyclopropyl derivatives (34, p. 519; 42). Like double bonds, cyclopropyl groups have been known to undergo addition (33, p. 1405) and to interact with carbonium ion centers. Rearrangements are commonly observed (23, p. 463).

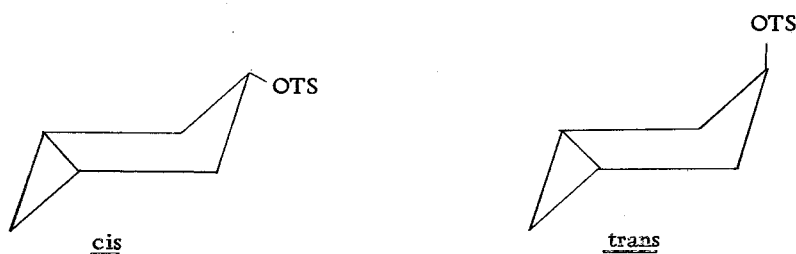


Many cases are known where molecules containing π electrons β to a function rearrange to α -functional cyclopropyl systems (15, p. 1936; 24, p. 314; 46; 49). This well known "homoallylic rearrangement" is exemplified below (50, p. 5795).

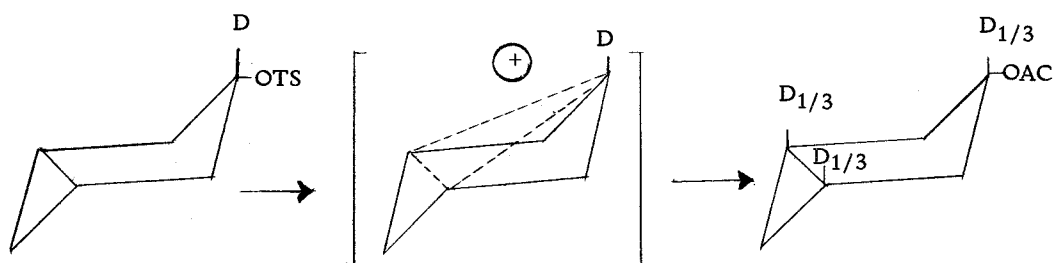


The enhanced solvolytic reactivity of cyclopropyl carbinyl compounds further testifies to their ability to interact with and stabilize a carbonium ion (2; 26, p. 320; 27, p. 2462; 41, p. 2509; 51, p. 3235).

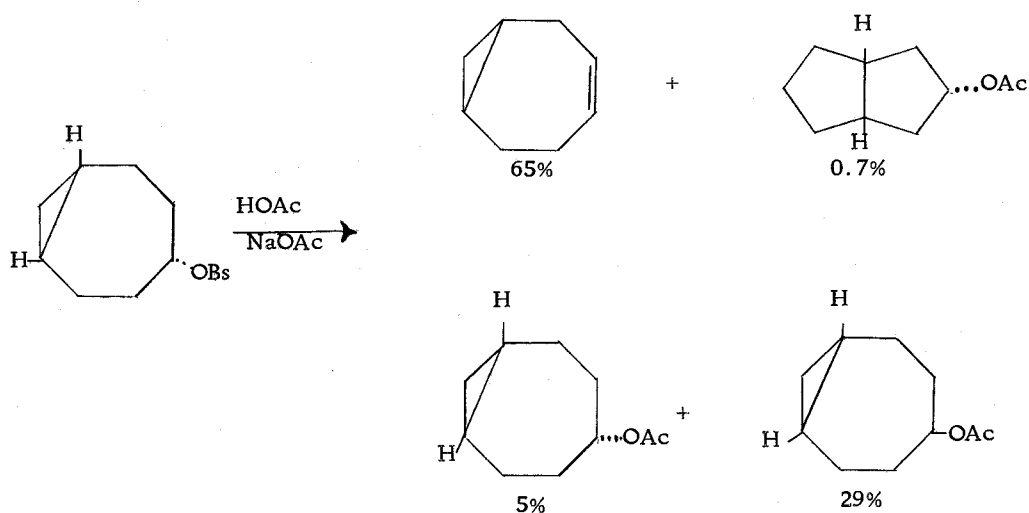
The work of Winstein and Sonnenberg on the 3-bicyclo [3. 1. 0] - hexyl tosylates is of special importance (51; 52).



The cis-isomer solvolyzes 30 times faster than the trans-, experiences complete retention of configuration, shows a special salt effect, and yields no olefin. The trans-isomer shows complete inversion and gives considerable olefin. Furthermore, the cis-isomer deuterated at C-3 gives complete scrambling between the one, three, and five positions of the cyclohexyl ring, whereas the trans-isomer shows very little scrambling (52). This evidence is all in agreement with cyclopropyl participation in the solvolysis of the cis-isomer and supports Winstein's non-classical "trishomocyclopropenyl cation" as an intermediate (52, p. 3244).



The observed capacity for cyclopropyl involvement with carbonium ions suggests that favorable geometry is the major requirement. The transannular proximity properties of the cyclooctyl system should also be favorable for this type of participation. Recently Cope solvolyzed some bicyclo [5. 1. 0] octyl brosylates and isolated the products. One pertinent case is given below (18, p. 4852).



A mechanism was proposed for formation of the endo-bicyclo [3. 3. 0] - oct-3-yl acetate which is in agreement with the stereochemistry. It involves cyclopropyl participation and a 1,2-hydride shift in a concerted process. They believe this to be the first example of participation by a cyclopropyl group which is remote from the initially formed

carbonium ion (18, p. 4853).

In conclusion, the interest in the synthesis of the bicyclo-[6.1.0]nonyl ring system was aroused because of the known peculiarities of the two interesting rings, cyclopropyl and cyclooctyl. In particular, bicyclo [6.1.0] non-4-ene is suspect of special proximity effects due to the transannular positions of the cyclopropyl group and the double bond.

DISCUSSION

The entire synthetic scheme, including derivatives, is illustrated by Figure II. Two different synthetic routes were followed to bicyclo [6. 1. 0] non-4-ene (III). Both routes started with 1,5-cyclooctadiene (I). The direct methylene addition by the Simmons-Smith reaction (44; 45) at first seemed especially convenient for this transformation since the product is obtained in a single step.

Bicyclo [6. 1. 0] non-4-ene (IIIa) by methylene addition.

The Shank and Shechter modification (43, p. 1826) of the Simmons-Smith reaction (44; 45) was employed. In this reaction methylene iodide in the presence of zinc-copper couple generates a cyclopropane ring from a double bond. Good yields are generally obtained with very little C-H insertion (29, p. 499; 32).

Two side products are possible from the reaction with cyclooctadiene.

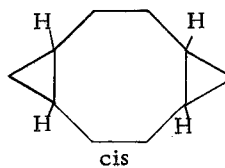
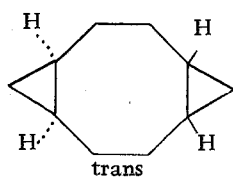
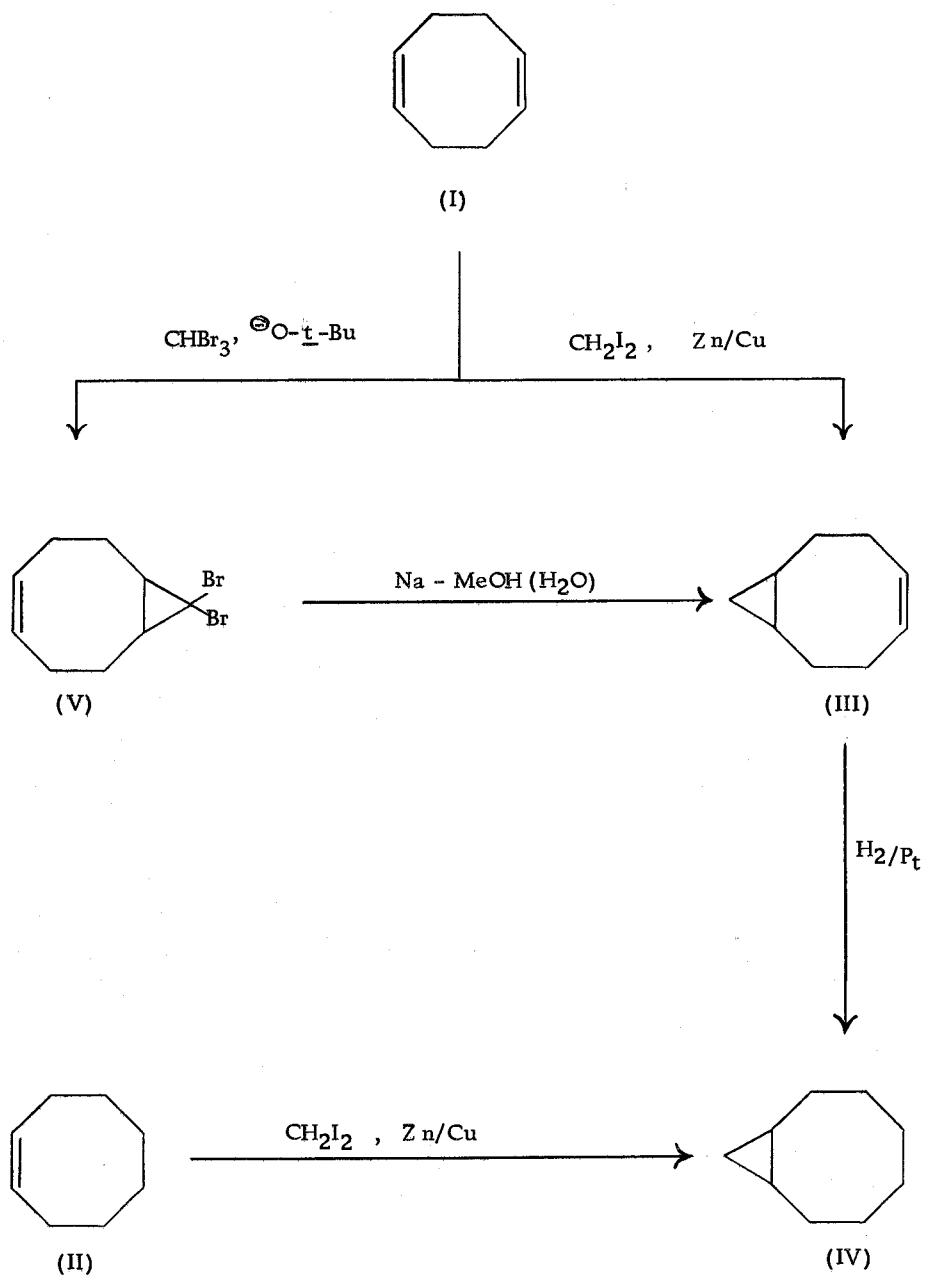


Figure II



Excess 1,5-cyclooctadiene (molar ratio 2:1; diene:methylene iodide) gave mostly bicyclo [6.1.0] non-4-ene (III). Vapor phase chromatography (v. p. c.) indicated only small amounts of side product. Cope and co-workers carried out this same reaction with a 2:1 molar ratio of methylene iodide to diene and obtained appreciable amounts of the tricyclodecanes (17, p. 4847).

Separation of the bicyclononene from unreacted cyclooctadiene was very difficult. Distillation through an efficient column and analysis of fractions by vapor phase chromatography showed contamination by 1,5-cyclooctadiene in all but one small fraction.

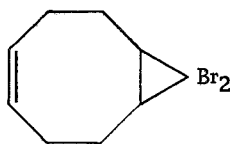
Bicyclo [6.1.0] non-4-ene (III) was identified from its physical properties, infrared spectrum and nuclear magnetic resonance (NMR) spectrum. It was definitely different than 1,5-cyclooctadiene according to vapor phase chromatography. The refractive index was reasonably close to the reported value. The infrared spectrum had peaks of medium intensity at 3065 and 1018 cm^{-1} which are characteristic of cyclopropyl compounds (1, p. 18, 29). The tricyclodecanes have cyclopropyl absorption at 3067 and 1020 cm^{-1} reported in the literature (32, p. 3125). Absorption at 1656 and 720 cm^{-1} testifies to the presence of the cis double bond in bicyclo [6.1.0] non-4-ene (1, p. 48). More evidence was provided by the nuclear magnetic resonance spectrum which had signals for

the vinyl hydrogens ($\tau = 4.4$) and the cyclopropyl hydrogen ($\tau = 10.2$).

Bicyclo [6. 1. 0] non-4-ene (IIIb) via dibromocarbene

Because of difficulties encountered in isolating and purifying the highly volatile bicyclononene, it was decided to prepare the mono-dibromocarbene adduct of 1,5-cyclooctadiene. The gem-dibromide could be readily separated from major contaminants by distillation because of its much higher boiling point. The bromine atoms could then be removed by sodium-methanol reduction. Winstein and Sonnenberg have prepared bicyclo [4. 1. 0] hept-3-ene in good yield by this route (51, p. 3240).

Using a slight excess of cyclooctadiene gave the dibromide (V) in 47% yield.

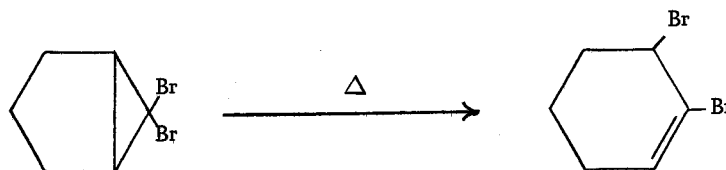


(V)

No reference to this compound was found in the literature so it was characterized carefully. The osmometer molecular weight and carbon and hydrogen analysis agree closely with this molecular

formula. A small peak in the infrared spectrum at 1655 cm^{-1} and a strong one at 700 cm^{-1} indicated the cis double bond (1, p. 48). The absorption at 745 cm^{-1} for the gem-dibromide is close to the 738 cm^{-1} peak reported for 6,6-dibromobicyclo [3.1.0]hexane (48, p. 750). The nuclear magnetic resonance spectrum was complex but did verify the presence of vinyl hydrogens.

Probably the most significant evidence supporting the gem-dibromide structure was the conversion to bicyclo [6.1.0] non-4-ene which has very characteristic cyclopropyl absorption in the infrared and nuclear magnetic resonance spectra. This additional evidence is essential because analogous dibromocarbene adducts have been known to rearrange upon heating. For example, 6,6-dibromobicyclo [3.1.0] hexane rearranges when distilled slowly (48, p. 750).



This is a particularly favorable rearrangement since the much less strained six membered ring is obtained. It is noteworthy that 9,9-dibromobicyclo [6.1.0] non-4-ene was distilled slowly at 90°C without rearrangement. The 9,9-dibromide reacts rapidly with silver

nitrate (alcoholic) as has been observed in analogous cases (47, p. 2024).

The sodium-methanol reduction of the 9,9-dibromide was accomplished in good yield. The product showed the same behavior as bicyclo[6.1.0]non-4-ene (IIIa) prepared from cyclooctadiene and methylene iodide, when examined by vapor phase chromatography. It was not obtained in completely pure form so the refractive indices did not check exactly. The infrared spectrum of this product (IIIb) had the characteristic cyclopropyl and cis double bond absorption. It was almost identical with the spectrum of the bicyclonene (IIIa) from the direct methylene addition.

Bicyclo[6.1.0]nonane

In order to establish completely the identity of bicyclo[6.1.0]non-4-ene, hydrogenation to the saturated bicyclo[6.1.0]nonane derivative was carried out. This compound is reported in the literature (25, p. 3160) and was prepared from cyclooctene by the methylene iodide and zinc-copper couple reaction. When these two products were obtained they proved to be identical according to vapor phase chromatography. Their infrared spectra were very similar, showing cyclopropyl absorption but no olefin peaks. The nuclear magnetic resonance spectrum showed cyclopropyl absorption at $\tau > 10$.

Summary of synthetic scheme

The scheme is illustrated by Figure II. Bicyclo[6.1.0]non-4-ene was obtained by two different routes. The fact that the products are identical is evidence supporting the structure of 9,9-dibromobicyclo[6.1.0]non-4-ene. Also bicyclo[6.1.0]nonane was obtained by two routes. This provides additional evidence for the structure of bicyclo[6.1.0]non-4-ene.

Acetolysis of bicyclo[6.1.0]non-4-ene

As mentioned previously, bicyclo[6.1.0]non-4-ene is expected to show some interesting transannular proximity effects. By analogy with some earlier work discussed in the historical section, it was suspected that these proximity effects might yield transannular products under solvolytic conditions.

When the acetolysis reaction was investigated, several products were obtained according to vapor phase chromatography. When the reaction was repeated, similar results were observed. There were at least eight major products, not all of which were completely resolved by vapor phase chromatography. The infrared spectrum indicated considerable ester (1735 cm^{-1}). After LiAlH_4 treatment, the infrared spectrum showed the ester had been

converted to alcohol (3365 cm^{-1}). An olefin band (1636 cm^{-1}) was also found which was probably present before LiAlH_4 treatment but could not be resolved due to interference from the carbonyl peak.

Due to the complexity of the mixture of acetolysis products and the difficulties involved in isolating the individual components, none of the products has been identified. This problem is not considered further in this thesis.

EXPERIMENTAL

Bicyclo[6.1.0]non-4-ene (III)A) From 1,5-cyclooctadiene and methylene iodide.

The procedure was adapted from the Shank and Shechter (43, p. 1826) modification of the Simmons-Smith reaction (44; 45). Subsequent to this work Cope reported the preparation of bicyclo-[6.1.0]non-4-ene by this same route (17, p. 4847). The cis-cis-1,5-cyclooctadiene¹ was distilled prior to use; b. p. 45-47°C (15 mm.), n_D^{21} 1.4918. Infrared spectrum: 2985, 2935, 2795, 1655, 1486, 1426, 1208, 1083, 1000, 800, 705 and 650 cm^{-1} . These properties are in accord with those in the literature (22, p. 482; 28, p. 915).

A mixture containing 56.4 g. (0.21 mole) of methylene iodide, 14.1 g. of freshly prepared zinc-copper couple (43, p. 1826), a trace of iodine and 45.3 g. (0.42 mole) of 1,5-cyclooctadiene in 165 ml. of anhydrous ethyl ether was heated under reflux for 44 hours. The cool mixture was filtered and the filtrate was washed successively with 3% hydrochloric acid, dilute sodium bicarbonate

¹ Provided through the courtesy of Cities Service Research and Development Company.

and water. The ethereal solution was dried over anhydrous calcium sulfate, filtered and the filtrate concentrated by carefully distilling the ether. The residue (58 g.) had an estimated composition of 22.6% ether, 43% cyclooctadiene, 31.4% bicyclo[6.1.0]non-4-ene and 3% of two minor products according to gas chromatography. The yield of monoadduct is thus 70%. Fractionation of the crude product on a 18" concentric tube column gave 1.30 g.; b. p. 90° C (100 mm.), n_D^{23} 1.4920. The major portion of the product was lost since no cold trap was used. Literature values; b. p. 75-85° C (22 mm.), n_D^{25} 1.4933 (17, p. 4847). Infrared spectrum: 3065, 3000, 2935, 2855, 1656, 1481, 1466, 1018, 970, 850 and 720 cm^{-1} . NMR spectrum: multiplet $\tau = 10.2$ (1H), triplet $\tau = 4.4$ (2H), multiplet $\tau = 9$ (5H) and a multiplet at $\tau = 8.8$ (6H).

B) From 9,9-dibromobicyclo[6.1.0]non-4-ene.

A procedure based on that developed by Winstein and Sonnenberg (51, p. 3240) was used. To a cooled solution of 25 g. (0.09 mole) of 9,9-dibromobicyclo[6.1.0]non-4-ene in 100 ml. of ethyl ether was added 35 g. (1.5 g. atom) of metallic sodium (in small pieces) over a four hour period. At the same time wet methanol (5 ml. of water in 150 ml. of methanol) was added dropwise to the vigorously stirred mixture. The mixture was stirred

another two hours, ether (25 ml.) was added, followed by more wet methanol (5 ml. of water in 100 ml. of methanol) and sodium (12 g. or 0.5 g. atom). After the mixture had been stirred an additional 2.5 hours, 175 ml. of water was carefully added followed by 25 ml. of ether. The aqueous layer was separated and extracted with pentane (3X75 ml.). The organic layers were combined, washed with water (4X25 ml.), dried over anhydrous calcium sulfate and filtered. The filtrate was concentrated by distilling the low boiling solvents. Fractional distillation of the residue gave 7.3 g. (0.06 mole) of bicyclo [6.1.0]non-4-ene (67% yield); b.p. 94-96°C (70 mm.), n_D^{25} 1.4891. Infrared spectrum: 3040, 3000, 1653, 1481, 1465, 1020, 970, 845 and 720 cm^{-1} . Vapor phase chromatography: retention time is the same as that of bicyclo[6.1.0]non-4-ene from cyclooctadiene and methylene iodide.

9,9-Dibromobicyclo[6.1.0]non-4-ene (V)

The dibromocarbene addition to 1,5-cyclooctadiene was accomplished by a method similar to that of Winstein and Sonnenberg (51, p. 3240). To a stirred solution of 100 g. (0.396 mole) of bromoform and 54 g. (0.5 mole) of 1,5-cyclooctadiene in 100 ml. of tert-butyl alcohol was added, over a period of ten hours, 594 ml. of 1.0 M potassium tert-butoxide in tert-butyl alcohol. The

mixture was kept cool during the addition and then allowed to stand at room temperature for 12 hours. Pentane (300 ml.) and water (500 ml.) was added and the mixture shaken. The organic layer was separated, washed with water (4X500 ml.) and concentrated by means of a rotary evaporator. Distillation of the residue gave 51.7 g. (0.185 mole) of light yellow liquid (47% yield); b. p. 70-73° C (0.2 mm.), n_D^{26} 1.5690 (colorless analytical sample). Infrared spectrum: 2995, 2915, 1655, 1481, 1435, 1093, 745 and 700 cm^{-1} . NMR spectrum: triplet near $\tau = 4$ (2H) and multiplets centered near $\tau = 7.7$ and 8.1. At this time the NMR instrument was not calibrated accurately. Treatment of the gem-dibromide with alcoholic silver nitrate gave instantaneous silver bromide precipitation.

Anal. Calc'd for $\text{C}_9\text{H}_{12}\text{Br}_2$: C, 38.60%; H, 4.32%; M. W. 280

Found: C, 38.43%; H, 4.26%; M. W. 279 (osmometer)

Bicyclo [6.1.0] nonane (IV)

A) From cis-cyclooctene and methylene iodide.

The general method of Shank and Shechter (43, p. 1826) was used. The cis-cyclooctene (obtained commercially) was distilled before use; b. p. 36° C (11 mm.), n_D^{21} 1.4695. Reported: b. p. 42° C (18 mm.), n_D^{25} 1.4682 (4, p. 3214). Infrared spectrum:

3005, 2895, 2835, 1651, 1464, 1446, 750 and 700 cm^{-1} .

A mixture containing 5 g. of freshly prepared zinc-copper couple (43, p. 1826), 20 g. (0.072 mole) of methylene iodide, 35 ml. of dry ether and a trace of iodine was heated to reflux until the iodine color disappeared (15 min.). Cyclooctene, 5 g. (0.05 mole), was carefully added. The stirred mixture was heated to reflux for 44 hours with the exclusion of atmospheric moisture. The crude product was isolated in the usual manner (45, p. 4262). Distillation gave 1.92 g. (0.015 mole) of clear liquid product (30% yield); b.p. $80-84^{\circ}\text{C}$ (49 mm.), n_D^{24} 1.4671. Literature values: b.p. 43°C (8 mm.), n_D^{25} 1.4622 (25, p. 3160). Infrared spectrum: 3045, 2975, 2895, 2835, 1481, 1464, 1446, 1030, 1005 and 845 cm^{-1} . NMR spectrum: multiplet near $\tau = 10.4$ and complex multiplets centered near $\tau = 9.4$ and $\tau = 8.4$. The NMR instrument was not calibrated accurately at that time.

B) From bicyclo [6. 1. 0] non-4-ene.

Bicyclo[6. 1. 0]non-4-ene, 1 g. (0.008 mole) in 15 ml. of pentane, was hydrogenated over platinum catalyst at 0°C and atmospheric pressure. Hydrogen consumption ceased at about 81% of the theoretical amount. The crude product was isolated by filtering the solution and carefully distilling the pentane out of the filtrate. The residue had the same retention time (v. p. c.) as

bicyclo [6. 1. 0] nonane from methylene iodide and cyclooctene. Infrared spectrum: 3020, 3000, 1465, 1027, 1004, 857, 843, 730 and 720 cm^{-1} ; n^{25}_D 1.4687. Reported: n^{25}_D 1.4622 (25, p. 3160).

Acetolysis of bicyclo [6. 1. 0] non-4-ene

The olefin was dissolved in dry acetic acid containing a small amount of p-toluenesulfonic acid. Atmospheric moisture was excluded while the solution was stirred and heated for several hours. The cool solution was poured into ice-water, the products extracted with pentane and the pentane solution washed successively with water, 5% sodium bicarbonate and water (until neutral to litmus). After the solution had been dried over anhydrous sodium sulfate, the pentane was distilled and the residue analyzed by vapor phase chromatography (v. p. c.).

A) Acetolysis I

A solution of bicyclo [6. 1. 0] non-4-ene (1 g. 99% pure by v. p. c.) in 100 ml. of acetic acid containing 1 g. of p-toluenesulfonic acid was heated to 80°C for ten hours. The crude products (isolation procedure described above) gave 11 v. p. c. peaks. Infrared spectrum (dilute CS_2 solution, compensated): 2895, 1735, 1436, 1375, 1025, 957 and 725 cm^{-1} . After treatment of the mixture with LiAlH_4 in ether, the material had an infrared spectrum (dilute CS_2 solution, compensated) with absorption at 3365, 2915, 1710 (small), 1636 (small), 1375, 1350, 1213 and 1045 cm^{-1} .

B) Acetolysis II

A mixture containing 2 g. bicyclo [6. 1. 0] non-4-ene (92% pure by v. p. c.), 1 g. p-toluenesulfonic acid and 100 ml. of dry acetic acid was heated to 50° C for 22 hours. The crude products (0.7 g.) showed 13 peaks (v. p. c.).

C) Acetolysis III

A 5 g. portion of bicyclo [6. 1. 0] non-4-ene (90% pure by v. p. c.) was dissolved in 200 ml. of acetic acid containing 1 g. of p-toluenesulfonic acid. The mixture was heated to 50° C for 29 hours. The crude product was isolated in the normal manner; 13 peaks (v. p. c.)

Molecular weight (osmometer)

The molecular weight of 9, 9-dibromobicyclo [6. 1. 0] non-4-ene was obtained using the Mechrolab vapor pressure Osmometer Model 301 with chloroform as solvent.

Infrared spectra

All spectra were obtained for the neat material unless otherwise indicated. The instrument was a Perkin-Elmer Model 21

infrared spectrophotometer equipped with a sodium chloride prism.

Nuclear magnetic resonance spectra

The Varian A-60 High Resolution NMR Spectrometer was used for all spectra. The material being studied was dissolved in CCl_4 containing tetramethylsilane as an internal standard.

Vapor phase chromatography

All analyses were run on the same 6' x 1/4" polyethylene glycol (carbowax 1500) column. A Perkin-Elmer Model 154C vapor fractometer was used with helium as carrier gas at 15 psi pressure. The results are listed in Table I using the following designations for the materials:

- (I) 1,5-cyclooctadiene.
- (II) cyclooctene.
- (IIIa) bicyclo[6.1.0]non-4-ene from methylene synthesis.
- (IIIb) bicyclo[6.1.0]non-4-ene from 9,9-dibromobicyclo[6.1.0]-non-4-ene.
- (IVa) bicyclo[6.1.0]nonane from methylene synthesis.
- (IVb) bicyclo[6.1.0]nonane from bicyclo[6.1.0]non-4-ene.

Table I

Vapor Phase Chromatography			
Sample	Temperature	No. of peaks	Retention times (min.) and area percentages of major peaks
I	162° C	1	3.8
II	152° C	1	2.9
IIIa	162° C	1	5.6
IIIb	162° C	2	5.8 (92%), 9.2 (6%)
IVa	162° C	1	3.5 (96%)
IVb	162° C	2	Pentane (near air peak), 3.3
I + IIIa	130° C	2	10 (54%), 14 (46%)
I + IIIa + IIIb	163° C	2	4.1, 5.9
IVa + IVb	162° C	2	Pentane (near air peak), 3.7
II + IIIa + IVa	162° C	3	2.3, 3.6, 5.1
Acetolysis #I	162° C	11	2.6, 3.6, 11, 14.1, 16.4, 18, 23, 26, 29, 39
Acetolysis #II	162° C	13	2.8 (19%), 3.8 (21%), 5.4 (9%), 19.6 (6%), 25.4, 28.2, 32.2, 36.8 (last 4, 42%)
Acetolysis #III	163° C	13	2.6 (15%), 3.5 (26%), 5 (33%), 8.3, 19, 24.5, 27.4, 31.5, 36 (last 6, 20%)

SUMMARY

1. Bicyclo [6. 1. 0] non-4-ene (III) was prepared by two different routes. The structure was established by the characteristic infrared spectrum, nuclear magnetic resonance spectrum and comparison with reported physical properties. As a final proof, bicyclo [6. 1. 0] nonane was prepared from the olefin (III) and compared with an authentic sample.
2. 9, 9-Dibromobicyclo [6. 1. 0] non-4-ene (V) was prepared and characterized. Proof of its structure was provided by analysis, infrared spectrum, nuclear magnetic resonance spectrum, and conversion to bicyclo [6. 1. 0] non-4-ene (III).
3. The acetolysis of bicyclo [6. 1. 0] non-4-ene was carried out and the products analyzed by v. p. c. At least eight major products were indicated.

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