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# The Preparation and Chemical Properties of Tetracyclo [3.3.0.0<sup>2</sup>,8.0<sup>4,6</sup>] Octan-3-One

Arnold G. Phillips

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THE PREPARATION AND CHEMICAL PROPERTIES OF  
TETRACYCLO [3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>] OCTAN-3-ONE

by

Arnold G. Phillips

A THESIS

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Graduate Division of Wayne State University, Detroit, Michigan  
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1963

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APPROVED BY:

Norman A. LeBel  
Advisor

11/12/63  
Date

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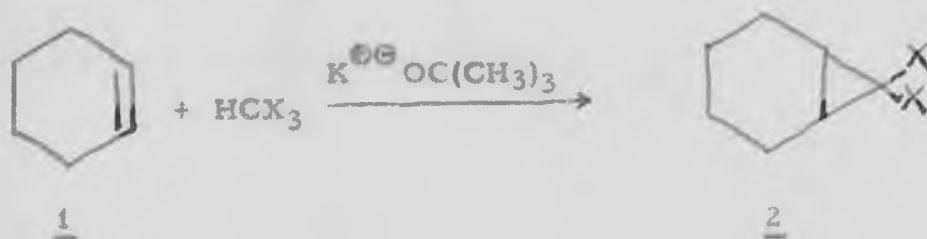
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# CHAPTER I.

## INTRODUCTION

Although carbene addition reactions have been known for a number of years, contemporary interest was revived by Doering and Hoffmann in 1954.<sup>1</sup> When a cooled mixture of cyclohexene and a saturated solution of potassium t-butoxide in t-butyl alcohol was treated with ethyl chloroformate, there was obtained a product (2, x = Cl), C<sub>7</sub>H<sub>10</sub>Cl<sub>2</sub>, in 40% yield. By employing alcohol-free potassium



t-butoxide, the yield was improved to 55%. The same reaction could be carried out with bromoform to give C<sub>7</sub>H<sub>10</sub>Br<sub>2</sub> in 75% yield.

Catalytic hydrogenation of 2 (x = Cl) gave methylcyclohexane (3). However, reduction of 2 (x = Br) with sodium in



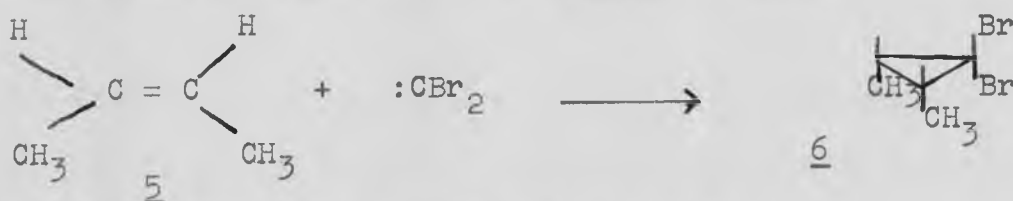

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<sup>1</sup>W. E. von Doering and A. K. Hoffmann, J. Am. Chem. Soc., **76**, 6162 (1954).

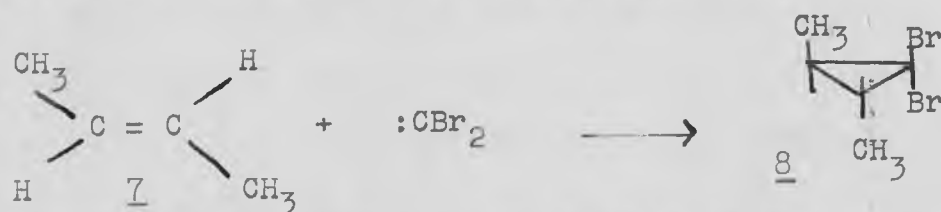
in alcohol afforded bicyclo [4.1.0] heptane (norcaradiene) (4):



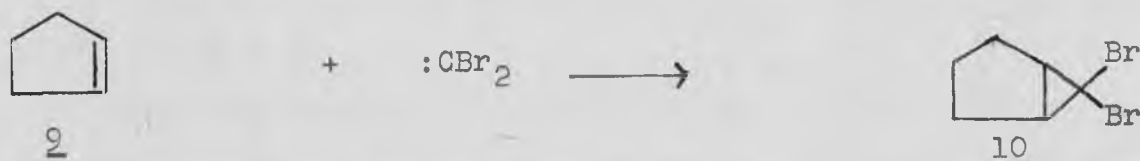
The reaction of dibromocarbene with 2-butene was found to be stereospecific;<sup>1</sup> cis-2-butene led to cis-1,1-dibromo-2,3-dimethylcyclopropane (6), and trans-2-butene afforded



trans-1,1-dibromo-2,3-dimethylcyclopropane (8).



The attempt by Sonnenberg and Winstein<sup>2</sup> to prepare a dibromocarbene adduct (10) of cyclopentene (9) resulted in

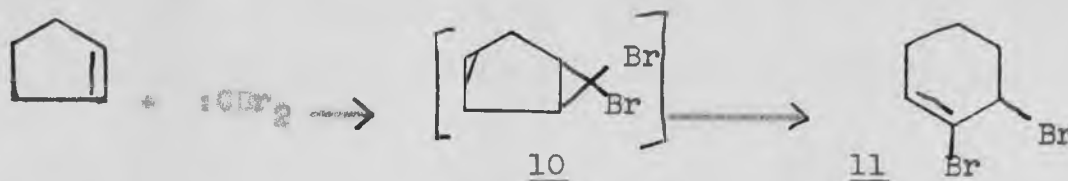


<sup>1</sup> P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., **74**, 3409 (1952).

<sup>2</sup> J. Sonnenberg and S. Winstein, J. Org. Chem., **27**, 748 (1962).



a liquid which boiled over a wide range, and which showed considerable variation in refractive index. Redistillation of this material, however, gave a constant boiling fraction whose properties agreed fairly well with those reported by Skell and Garner<sup>1</sup> for 11. The compound was shown to have the structure 2,3-dibromocyclohexene (11). This assignment was



verified by a correct analysis for  $C_6H_8Br_2$ ; unsaturation was indicated by the infrared spectrum, and cyclohexene was produced upon reduction with sodium in methanol.

It should be pointed out that the expected adduct, 6,6-dibromobicyclo [3.1.0] hexane (10), can be obtained from the reaction of cyclopentene and dibromocarbene if the mixture is distilled rapidly at low temperature. However, when the adduct is heated for a short time in the absence of solvent at  $155^\circ$ , it readily isomerizes to the rearranged product 11.

Mechanistically, the formation of a dihalocarbene can be thought of as occurring by way of a multi-step process.<sup>2</sup>

<sup>1</sup> P.S. Skell and A.Y. Garner, J. Am. Chem. Soc., **74**, 3409 (1952).

<sup>2</sup> R.E. von Doering and A.K. Hoffmann, J. Am. Chem. Soc., **76**, 6162 (1954).

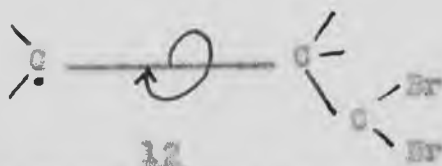
First a proton is removed from the haloform to produce the trihalomethide ion (eq. 1).



The second step consists of a rate determining loss of halide ion from the trihalomethide ion to generate the dihalocarbene, which can subsequently add to the olefin (eq. 2 and 3).



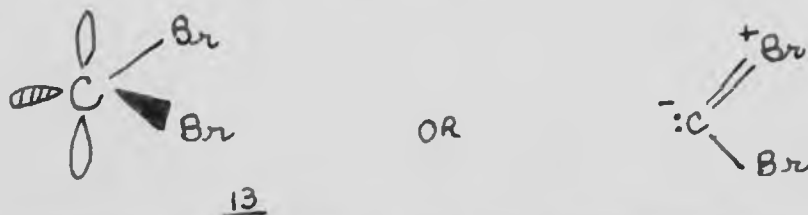
With regard to the cyclization process itself, however, two possibilities may be visualized concerning the nature of the intermediate: (1) a cyclopropane structure in which bond formation to both carbon atoms was established simultaneously or (2) a diradical (cf. 12) with propane bond angles and bond lengths.



If the latter formulation is correct, the relative reaction rates of  $\text{:CHBr}_2$  and  $\cdot\text{CCl}_3$  with a series of olefins should

be similar, provided the diradical structure has a lifetime longer than a normal vibration period ( $\sim 10^{-13}$  seconds). Interaction between the trivalent carbon atoms over a distance of 2.54 Å (the  $C_1 - C_3$  distance in propane) should make only a minor contribution to the ground state of the structure, and whatever structural factors operate to make one olefin more reactive than another in the addition of  $\cdot CCl_3$  should operate equally well in the addition of  $:CBr_2$ . This explanation has been rejected for two reasons:<sup>1</sup> (1) the failure to obtain a reactivity series characteristic of the reaction of olefins with the trichloromethyl radical, and (2) the complete stereospecificity of the reaction of cis- and trans-2-butene with dibromocarbene.

According to Skell and Garner,<sup>2</sup> carbenes may be described as compounds with the planar carbenium ion structure, in which two electrons fill an  $sp^2$  orbital leaving a single unoccupied  $p$ -orbital. This would provide substantial stabilization of the singlet state of the dibromocarbene species by overlap of the  $p$ -orbital (cf. 13) with the filled  $p$ -orbitals of the bromine atoms. However, all carbene species have been



<sup>1</sup> F. S. Skell and A. Y. Garner, J. Am. Chem. Soc., **78**, 5430 (1956).

<sup>2</sup> Ibid.

examined with EPR show triplet, i.e., diradical, ground states. These latter observations provide no evidence as to the reactive states of such species.<sup>1,2</sup>

In the reaction of a carbene with an olefin, bonding in the transition state may be considered a result of overlap of the vacant p-orbital of the carbene with the  $\pi$ -orbital of the olefin. Maximum overlap should take place if the carbene lies above the olefin in a plane parallel to the plane of the double bond (and probably closer to one than to the other of the olefinic carbon atoms) (14). The stereospecific-



ity of the dihalocarbene additions has shown that there must be nearly simultaneous bonding to both atoms of the unsaturated linkage. It is now possible to conclude that the stereospecific manner in which a dihalocarbene adds to an olefin is consistent with the intermediate complex shown in equation 4.



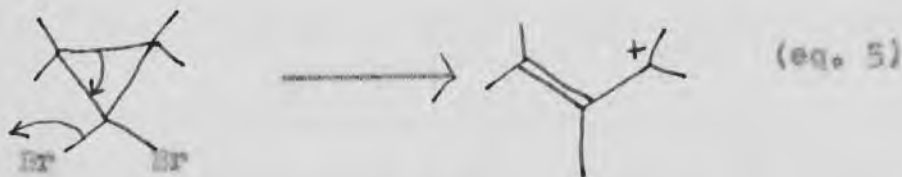
<sup>1</sup>A.M. Trozzolo, R.W. Murray, O. Smolinsky, W.A. Yager, and E. Wasserman, J. Am. Chem. Soc., **85**, 2526 (1963).

<sup>2</sup>A.M. Trozzolo, R.W. Murray, and E. Wasserman, J. Am. Chem. Soc., **84**, 4991 (1962).

This complex may be considered as a partially formed cyclopropane that has developed carbonium ion on one of the carbon atoms of the double bond which subsequently collapses within the lifetime of one molecular vibration to the cyclopropane structure. As the transition state passes on to the cyclopropane product the carbene moiety (atoms C, X and X) must rotate into a plane perpendicular to the plane originally defined by the double bond.

Furthermore, it has been shown that the intermediate complex in equation 4 has a greater affinity (14 times) for olefin than for bromine. This would suggest that this intermediate has more carbonium ion character than does an intermediate complex of an olefin-bromination reaction.<sup>1</sup>

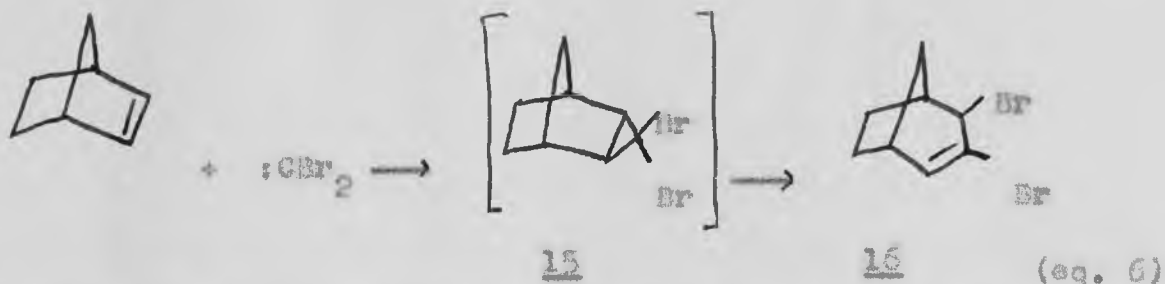
As previously mentioned, 2,2-dibromobicyclo [3.1.0.] hexane will rearrange, upon heating, to 2,3-dibromocyclohexene. In fact, this species is two-hundred times<sup>2</sup> more reactive than the analogous 2,2-dibromobicyclo [4.1.0.] heptane. The driving force for the rearrangement is postulated as being derived from the relief of strain in open- in the cyclopropane ring (equation 5).



<sup>1</sup>P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., **78**, 5430 (1956).

<sup>2</sup>P. S. Skell and S. R. Sandler, J. Am. Chem. Soc., **80**, 2024 (1958).

With this in mind, one can readily see application of this synthetic procedure to norbornylene (equation 6).



The rearranged adduct (16) has been reduced with lithium aluminum hydride, and the resulting vinyl bromide has been hydrolyzed to bicyclo[3.2.1] octan-3-one.<sup>1,2</sup>

Original work on this system was done by Bergman,<sup>3,4</sup> followed by the investigations of Jefford,<sup>5</sup> Ghosez and Laroche,<sup>6</sup> and recently Moore, Moser, and LaPrade.<sup>7</sup> That rearrangement of the dihalocarbene adducts of norbornylene should take place readily is made clear by an examination of a molecular model (17).

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<sup>1</sup>

K. Adler and R. Reubke, Ber., 91, 1525 (1958).

<sup>2</sup>

P. von Schleyer and S. Nicholas, Abstracts, 140th Meeting, Am. Chem. Soc., Chicago, September 3-8, 1961, 752.

<sup>3</sup>

E. Bergman, Abstracts, 142nd Meeting, Am. Chem. Soc., Atlantic City, N.J., September 9-14, 1962, 979.

<sup>4</sup>

E. Bergman, Shell Chemical Company Publication P-1132.

<sup>5</sup>

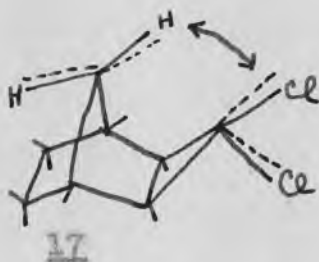
W. Jefford, Proc. Chem. Soc., February (1963), p. 64.

<sup>6</sup>

L. Ghosez and P. Laroche, Proc. Chem. Soc., March (1963), p. 90.

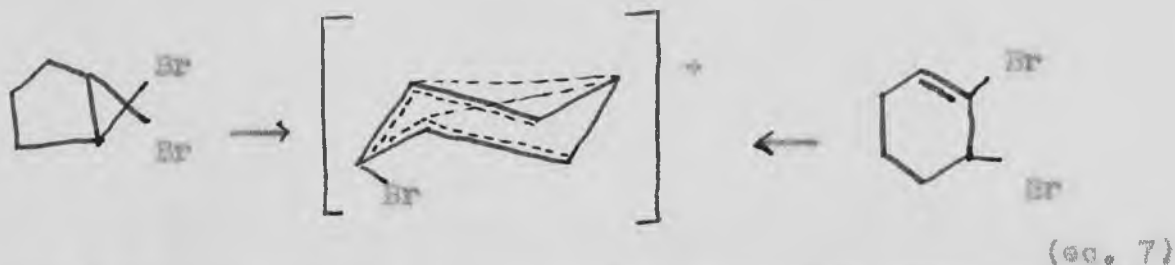
<sup>7</sup>

W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., 28, 2200 (1963).



Repulsion between the syn-C-8 proton (syn to the  $\text{CCl}_2$ ) and the cis-C-3 chlorine is readily visualized. Rocking of the C-8 methylene group away from the chlorine atom must be accompanied by substantial bond angle deformation. Nuclear magnetic resonance shows this proximity of the cis-C-3 chlorine atom to the syn-C-8 hydrogen atom. The latter is strongly deshielded by the chlorine atom and resonance occurs at  $2.15 \delta$ , whereas the anti-C-8 proton must result from it being forced into a high shielding environment.

During the rearrangement, which occurs upon distillation of the adduct, an intense, fairly stable purple color has been observed. An explanation involving an extended homocyclopropenyl cation as proposed by Winstein<sup>1,2,3,4</sup> has been offered, which is analogous to the following system (eq. 7).



<sup>1</sup> S. Winstein and J. Sonnenberg, J. Am. Chem. Soc., **83**, 3235 (1961).

<sup>2</sup> Ibid., **83**, 3244 (1961).

<sup>3</sup> S. Winstein, J. Sonnenberg, and L. DeVries, J. Am. Chem. Soc., **81**, 6523 (1959).

<sup>4</sup> Ibid., **81**, 6524 (1959).



Hofmann and co-workers<sup>1</sup> have synthesized 7,7-dibromonorcar-3-ene in 70% yield by a dibromocarbene addition to cyclohexa-1,4-diene. When applied to norbornadiene (18), this synthesis led (via original adduct 19) to 3,4-dibromobicyclo [3.2.1] octa-2,6-diene (20).<sup>2</sup>



The nortricycyl system, which will now be discussed, has been known for some time. Many reports have dealt with methods of synthesis and relative stability. Discussion will be limited to 3-nortricyclanone and related analogs.

In the course of a structure proof of 3-nortricyclanone (21), Cristol and co-workers<sup>3</sup> noted its stability to sodium amide in refluxing dioxane. On the other hand, similar treatment of dehydronorcamphor (22) led to a rapid and

21

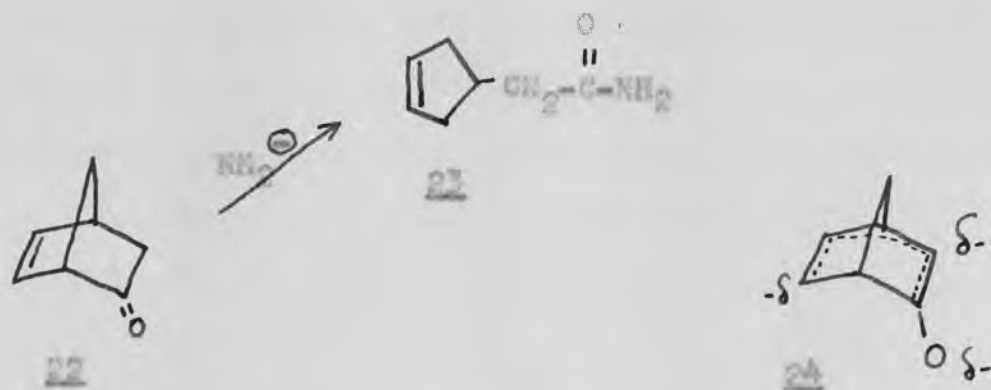
<sup>1</sup> K. Hofmann, S.F. Orochena, S.M. Sax, and G.A. Jeffrey, J. Am. Chem. Soc., 81, 992 (1959).

<sup>2</sup> W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., 28, 2200 (1963).

<sup>3</sup> S.J. Cristol and P.K. Freeman, J. Am. Chem. Soc. 83, 4427 (1961).

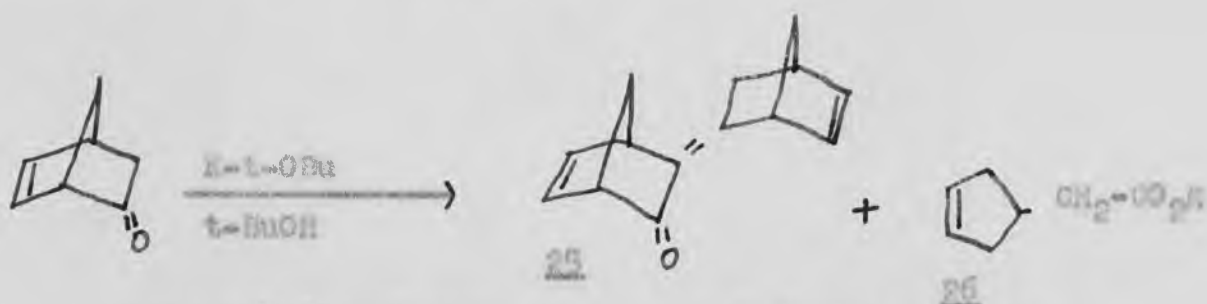


quantitative isomerization to  $\Delta^3$ -cyclopentenylacetamide (23).



These results suggested that 21 and 22 could not be interconverted via a resonance stabilized homoenolate anion such as 24.

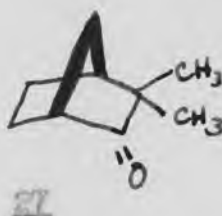
Cristol tested the hypothesis that perhaps a more bulky base might be unable to attack the carbon atom of the carbonyl group and thus be forced to react with an  $\alpha$  hydrogen. Dehydronorcamphor was allowed to react with a *t*-butyl alcohol solution of potassium *t*-butoxide. There was obtained 31% of the condensation product, 3-dehydronorbornylidenedehydronorcamphor (25) and 19% of  $\Delta^3$ -cyclopentenylacetic acid.



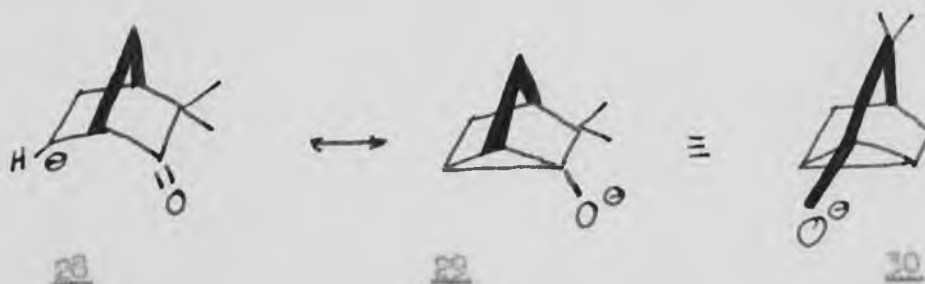
That an hydrogen atom  $\alpha$  to a carbonyl group is acidic, and that its removal by a base will afford an

enolate anion are both well-known facts. The enolate is stabilized by resonance conjugation with a neighboring  $\pi$  electron system. Homoenjugation might be anticipated to aid in the removal of an hydrogen more remote from a carbonyl group thereby leading to an homoenolate anion.

A case in point is (+) camphenilone (27) in which there are no enolizable hydrogens in the usual sense.



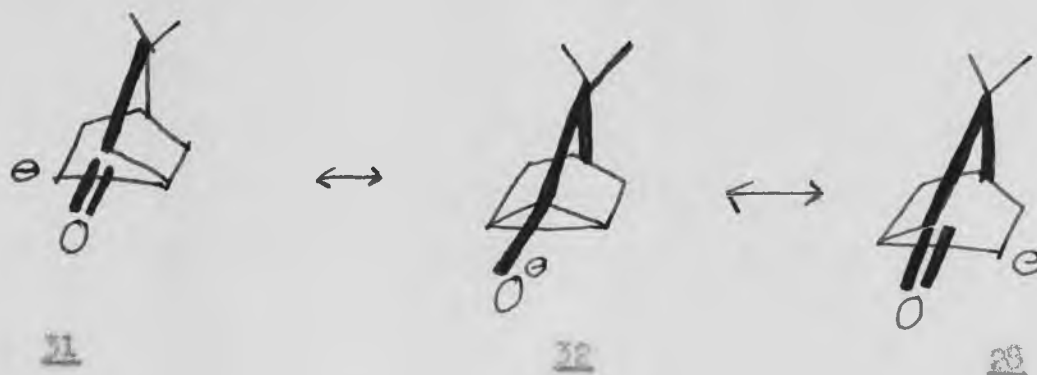
However, (+) camphenilone is racemized when heated with potassium t-butoxide in t-butyl alcohol. This racemization has been explained by abstraction of an hydrogen atom at C-6 to form a homoenolate anion,<sup>1</sup> in which the charge is stabilized by delocalization to the carbonyl group (eq. 8).




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<sup>1</sup>  
A. Nikon and J.L. Lambert, J. Am. Chem. Soc., 84,  
3526 (1962).

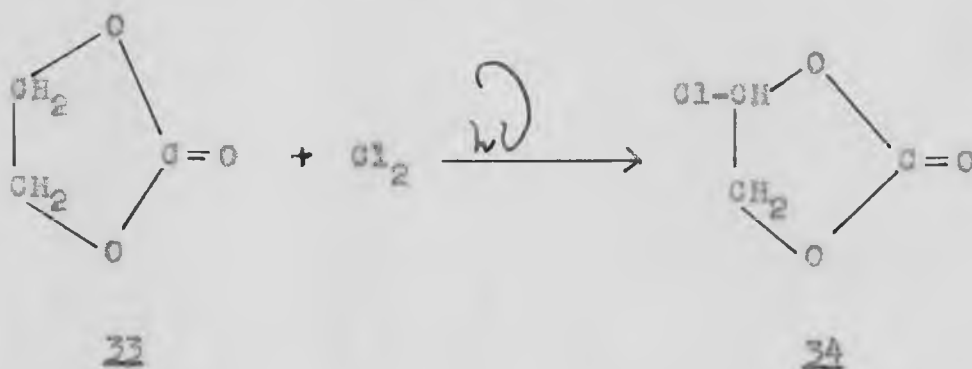
The ion species 30 is symmetrical and the system loses its optical activity. The symmetrical nature of the homocyclate anion itself can be illustrated by the three canonical structures 29, 31, and 32.



## CHAPTER II.

### RESULTS AND DISCUSSION

The original aim of this project was a synthesis and study of the properties of bicyclo[3.2.1] oct-6-ene. A sequence of reactions leading to this material was outlined and which involved endo-cis-bicyclo[2.2.1]-hept-5-ene-2,3-diol as a precursor. Ethylene carbonate (31) was photochemically chlorinated<sup>1</sup> to the mono-chloro compound (34). The product was obtained in the



pure state, but in lower yields than that reported in the literature.<sup>2</sup>

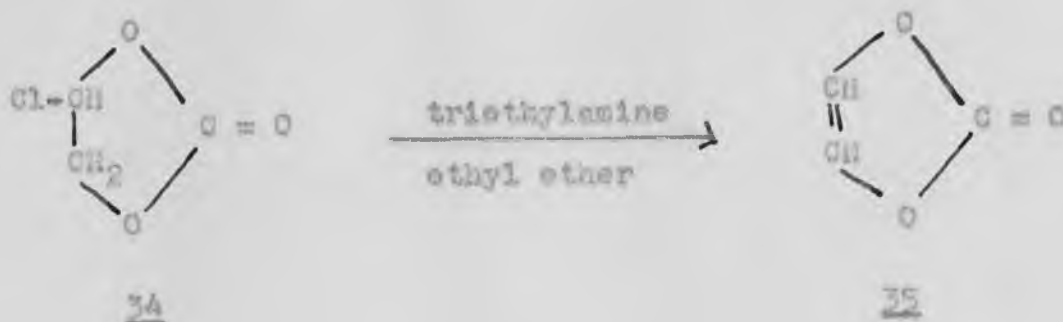
Subsequent dehydrohalogenation with triethylamine<sup>3</sup> gave vinylene carbonate (35). Vinylene carbonate has been

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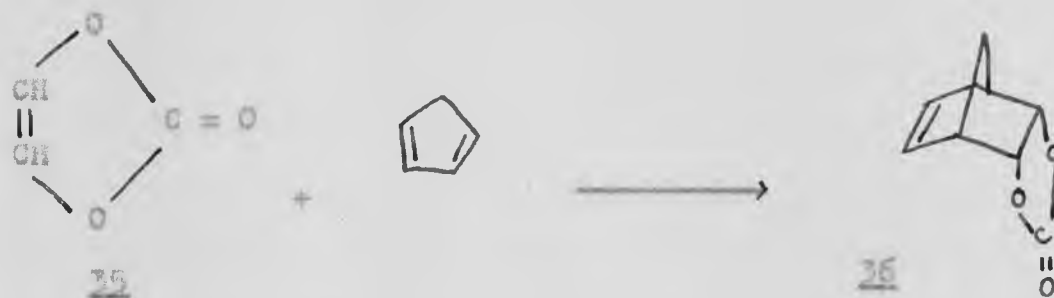
<sup>1</sup> H.S. Newman and R.W. Addor, J. Am. Chem. Soc., **75**, 1264 (1953).

<sup>2</sup> Ibid.

<sup>3</sup> H.S. Newman and R.W. Addor, J. Am. Chem. Soc., **77**, 379 (1955).



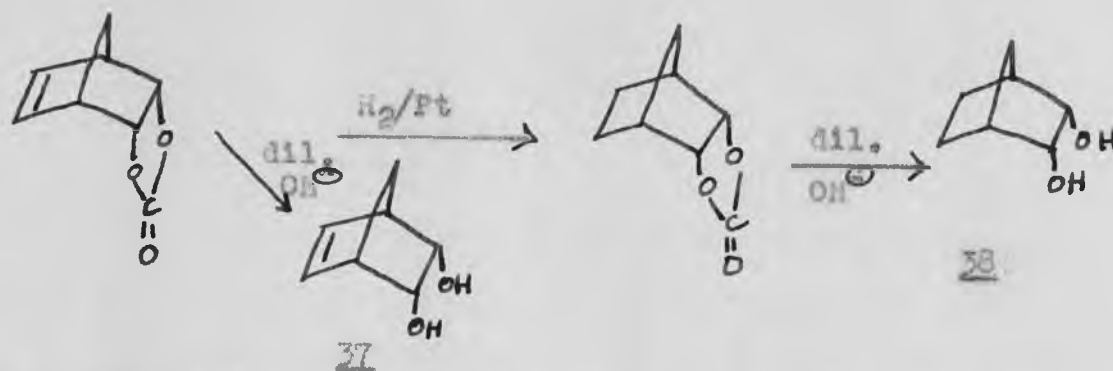
employed as a dienophile in several Diels-Alder reactions. With cyclopentadiene as the diene component, an adduct has been obtained, and was assigned the endo-cis- configuration (36).<sup>1</sup>



This addition was repeated, and distillation of the adduct afforded a semi-solid which was most difficult to crystallize. It was not possible to obtain a sharper melting product. Alkaline hydrolysis of the adduct<sup>2</sup> would be expected to lead to endo-bicyclo [2.2.1] hept-5-ene-2,3-

<sup>1</sup> K. Adler and G. Stein, Angew. Chem., 50, 510 (1937).

<sup>2</sup> H. Kwart and W. B. Vosburgh, J. Am. Chem. Soc., 76, 5400 (1954).



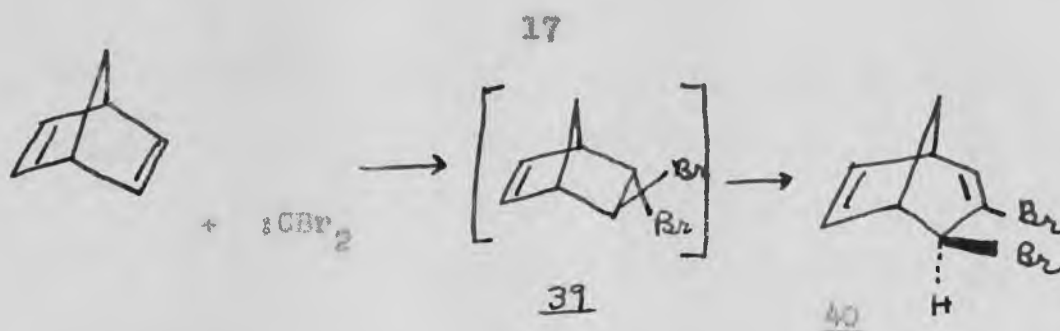
diol (37). The hydrogenated adduct has been converted to the corresponding endo-cis-saturated diol (38).<sup>1,2</sup> Newman has reported the formation of the unsaturated diol by dilute alkaline hydrolysis of the adduct, and noted the difficulty in obtaining a sharply melting product. Alkaline hydrolysis of the adduct prepared in our work gave a liquid which indicated a very weak test for unsaturation with bromine in carbon tetrachloride. This product could not be hydrogenated, nor did its infrared spectrum indicate the presence of a double bond.

At this point, a different approach to the synthesis of the bicyclo[3.2.1]octenone system was studied. The product formed from dibromocarbene addition to norbornadiene was found to be predominantly exo-2,3-dibromobicyclo[3.2.1]octa-2,6-diene (40).<sup>3</sup>

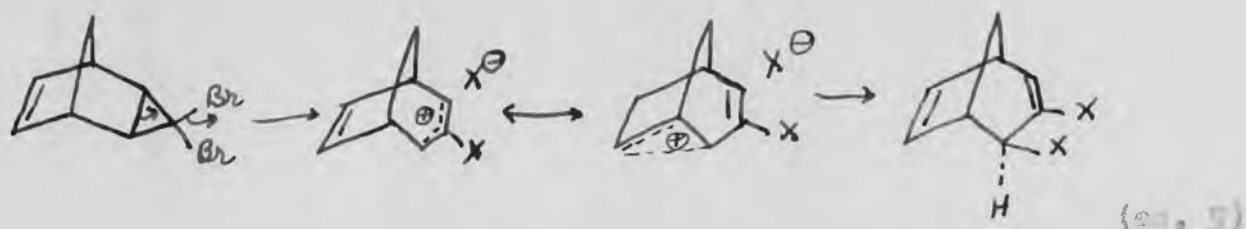
<sup>1</sup> H. Kwart and W.G. Vosburgh, J. Am. Chem. Soc., 76, 5400 (1954).

<sup>2</sup> Ibid., 76, 4072 (1954).

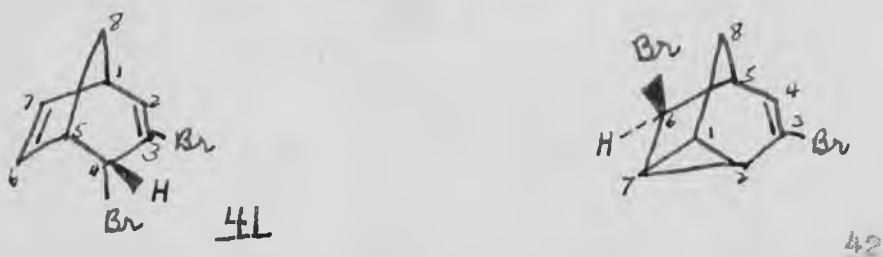
<sup>3</sup> W.R. More, W.R. Moser, and J.R. LaPrade, J. Org. Chem., 28, 2200 (1963).



The dihalocyclopropane intermediate 39 immediately rearranges to the dihalocycloolefin. Moore has suggested<sup>1</sup> that the intermediate might well be a tight ion pair (cf. eq. 9).



In addition to 40, both the endo- epimer 41 and a tricyclic vinyl bromide 42 are formed.<sup>2</sup>



The three products, exo : endo : tricyclic, were obtained in the ratio 83 : 11 : 6.<sup>3</sup> The exo- and endo- epimers can be distinguished by their nuclear magnetic resonance spectra.

<sup>1</sup> W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., **28**, 2200 (1963).

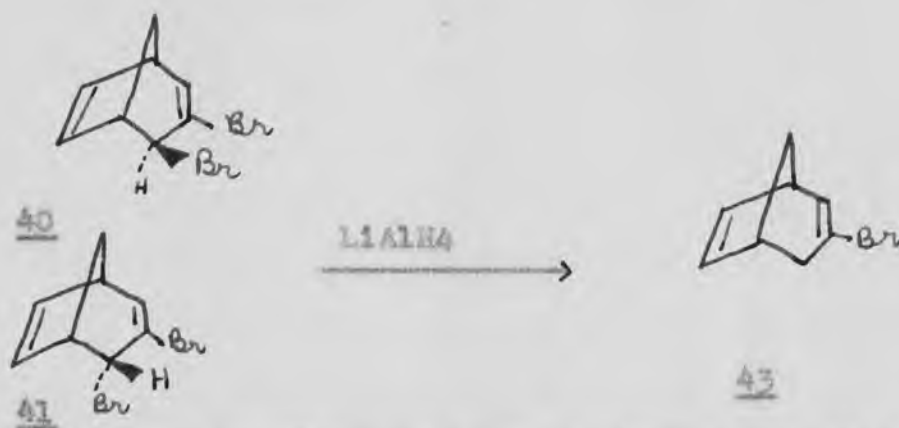
<sup>2</sup> Ibid.

<sup>3</sup> Ibid.

The C-4 proton of 40 appears as a doublet at 4.44  $\delta$ ,  $J = 2.0$  c.p.s.; but in the endo- configuration (41), the C-4 proton appears as a doublet at 4.89  $\delta$ ,  $J = 5.0$  c.p.s. The C-6 bromine atom in 42 has been assigned an exo-orientation.<sup>1</sup>

We have repeated this reaction of dibromocarbene with norbornadiene, and have confirmed these results.

Lithium aluminum hydride reduction of a mixture of 40 and 41 led to removal of the allylic bromine atom.<sup>2</sup> An isomer-free vinyl bromide 43 was obtained and characterized.



Moore has reported that the tricyclic dibromide 42 also gives 43 upon lithium aluminum hydride reduction.<sup>3</sup> The

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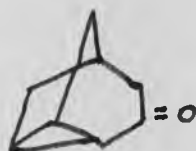
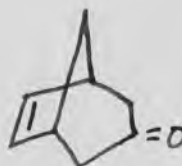
<sup>1</sup> W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., **28**, 2200 (1963).

<sup>2</sup> Ibid.

<sup>3</sup> Ibid.



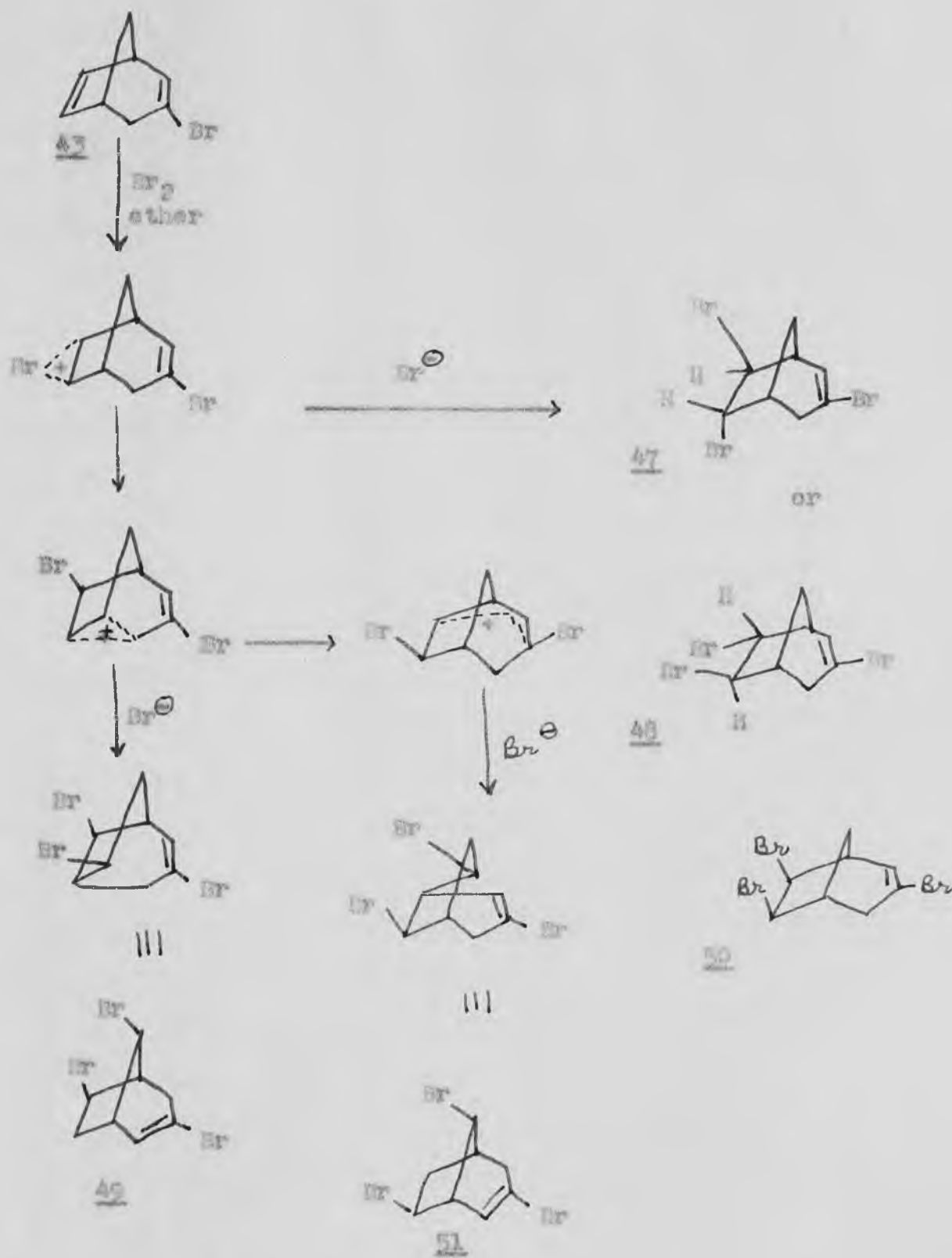
The tricyclic bromide 44 was not detected.

454446

Base-catalyzed hydrolysis of 43 was unsuccessful, and acid hydrolysis of this species was not attempted. However, Moore has carried out the hydrolysis of 43 with 80% aqueous sulfuric acid, and succeeded in isolating the tricyclic ketone 45 in poor yield.<sup>1</sup> Bicyclo [3.2.1] oct-6-en-3-one (46) was not detected.

It then became apparent that monobromide 43 would not be a suitable precursor for the production of ketone 46. Therefore, the reactive double bond of 43 was protected by formation of a tribromide. Bromination of 43 at low temperature in ether solution afforded a white, crystalline tribromide in good yield. This compound was found to be quite heat sensitive if slightly impure. Elemental analysis was consistent with the formula  $C_8H_9Br_3$ , and infrared and nuclear magnetic resonance spectra confirmed the presence of a vinyl bromide. At least five possibilities are indicated for the structure of this tribromide. These are given as 47, 48, 49, 50, and 51 in Scheme I which outlines the possible mechanisms of formation.

<sup>1</sup> W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., **28**, 2200 (1963).

SCHEME 1

The nuclear magnetic resonance spectrum of the tribromide is reproduced in Figure 2. Although it is difficult to arrive at a firm conclusion regarding its structure, the fact that one of the protons attached to a carbon atom bearing a bromine substituent shows as a singlet (4.4  $\delta$ ) seems to preclude structures 47, 48, and 50 from consideration. At this time, no choice between 49 and 51 can be made.

Base-catalyzed hydrolysis of the tribromide was unsuccessful. The tribromide was also found to be quite resistant toward acid-catalyzed hydrolysis. However, when the compound was stirred at 50° for 24 hours with a sulfuric acid - water - ethanol (1.4 : 1 : 2 by volume) system, a substance was isolated whose infrared spectrum showed strong carbonyl absorption as well as absorption in the 3  $\mu$  region. No bands were detected indicating unsaturation, and qualitative tests for unsaturation were negative. The ketone was a white, crystalline solid which could readily be sublimed, and elemental analysis was consistent with a formula  $C_8H_8O$ . Polymerization occurred upon prolonged standing at room temperature. The 2,4-dinitrophenylhydrazone was formed immediately upon addition of the reagent, and showed the correct analysis.

The infrared spectrum of the ketonic product shows carbonyl absorption at 1725  $cm^{-1}$ , and the ultraviolet spectrum gives  $\lambda_{max}^{C_2H_5OH} = 281 m\mu (\epsilon = 51)$ . These data are indicative of a normal cyclohexanone structure. The nuclear

magnetic resonance spectrum (Figure 3) confirmed the absence of vinyl hydrogens; complex multiplets occur in the region 1.3 - 2.6  $\delta$ . The structure of the ketone was thus tentatively assigned as tetracyclo [3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>] octan-3-one (52). Support for this assignment is given by the mass spectrum (Figure 4). The molecular weight is confirmed by the mass ion peak at  $m/e = 120$ . Loss of the elements of carbon monoxide would give rise to the  $M - 28$  peak (tropilidene or norbornadiene mass ion) and the  $M - 29$  peak must correspond to tropilidene or norbornadienyl cation. The metastable peak at  $m/e = 70.6$  is not unexpected and arises from the two peaks at  $m/e = 120$  and 91. The remainder of the spectrum corresponds closely to that of norbornadiene and quadricyclene<sup>1</sup> and provides strong confirmatory evidence for the assigned structure.

A possible mechanism for formation of the tetracyclic ketone is given in Scheme II. The method of formation suggests unusual stability for this unique ring system.

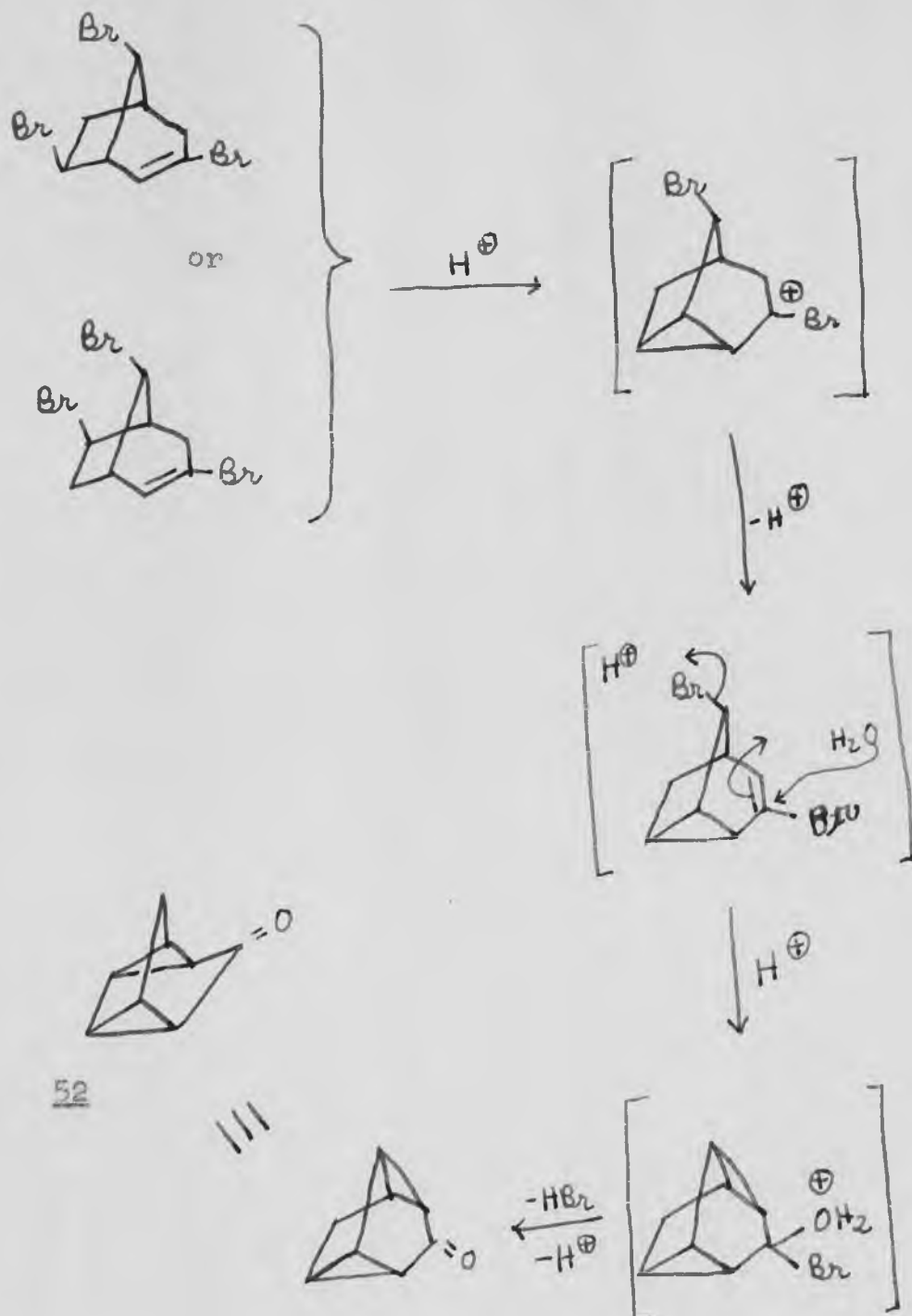
Sodium borohydride reduction<sup>2</sup> of the ketone gave an

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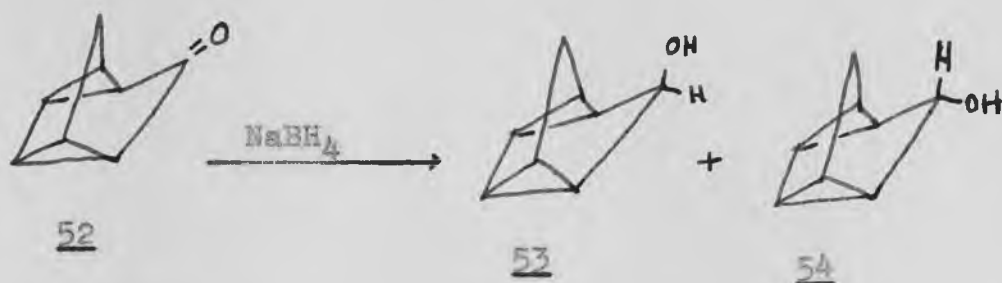
<sup>1</sup>  
Z. Dolejack, V. Samus, and H. Prinzback, Angew. Chem., Int. Ed., **1**, 598 (1962).

<sup>2</sup>  
A.C. Cope, J.M. Grisar, and P.E. Peterson, J. Am. Chem. Soc., **82**, 4299 (1960).

SCHEME II



alcohol. Gas chromatographic analysis indicated that two isomers corresponding to a mixture of the epimeric exo- and endo- alcohols were present.



Oxidation<sup>1</sup> of the mixture of the two alcohols gave a partial conversion to a ketone whose infrared spectrum, retention time on gas chromatography, and 2,4-dinitrophenylhydrazone derivative were identical with that of the authentic ketone (52). This evidence lends support to the postulate that the alcohols are epimeric at C-3.

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<sup>1</sup>  
A.C. Cope, S. Moon, and P.E. Peterson, J. Am. Chem. Soc., 84, 1928 (1962).

N. M. R. spectrum of  
3-bromobicyclo [3.2.1]-  
octa-2,6-diene.

416.6

25

τ-6.1-6.5δ

τ-1.5-2.9δ

Figure 1.

N. M. R. spectrum of  
3,6,8-tribromobicyclo-  
[3.2.1] oct-2-ene.

431.4



K-2.0-3.16

4.25  
1 to 1  
4.45

6.05  
1 to 1  
6.25

FIGURE 2.



N.M.R. spectrum of  
tetracyclo [3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]-  
octan-3-one.

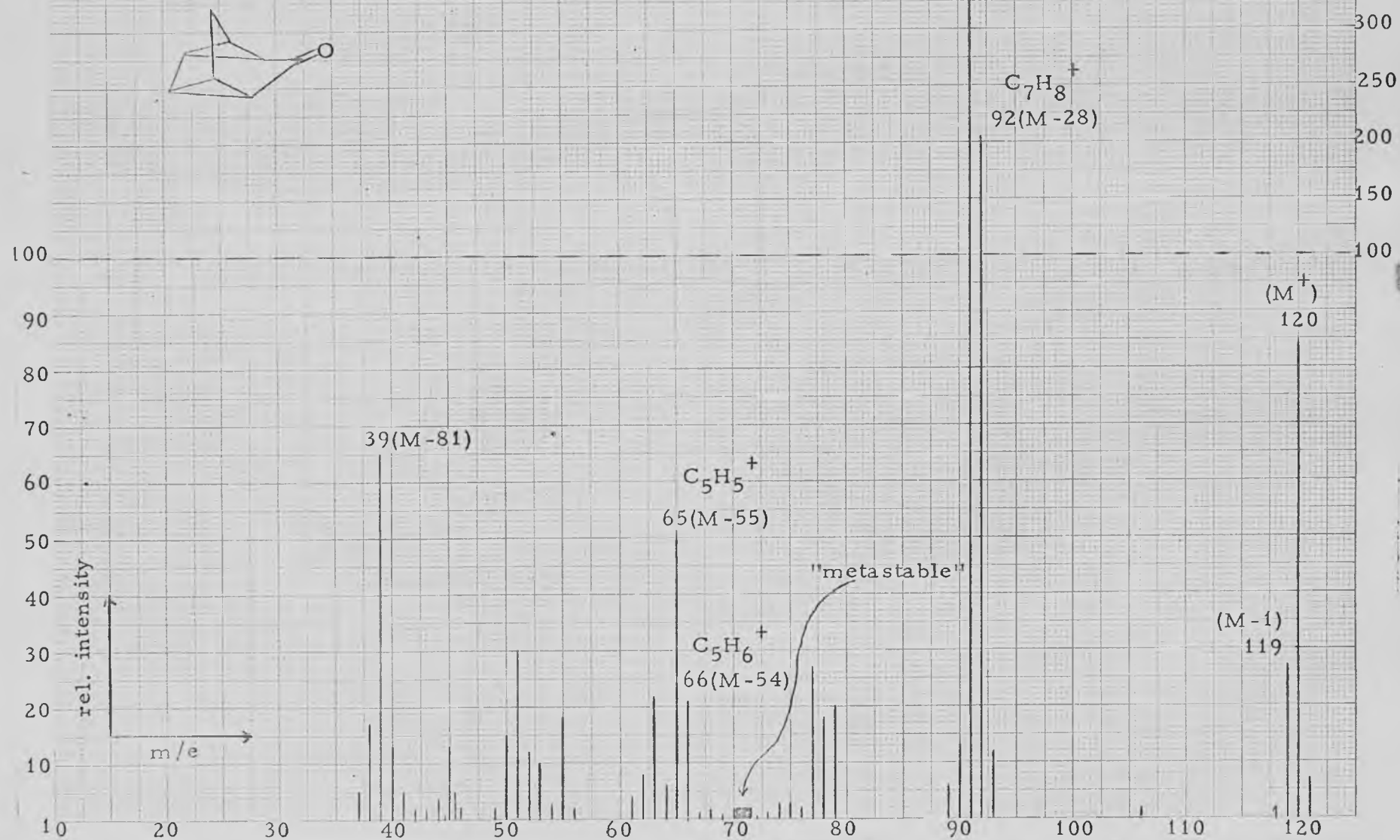
170.8

1.3 TO 2.6  $\delta$

FIGURE 3.

MASS SPECTRUM OF  
Tetracyclo[3.3.0.0.<sup>2,8</sup>0.<sup>4,6</sup>]octan-3-one

FIGURE 4



### CHAPTER III.

#### EXPERIMENTAL<sup>1</sup>

Gas Chromatographic Analysis. - The gas chromatography column employed for these experiments consisted of a 6' x 8 mm. pyrex tube packed with 15% by weight of polyglycol K-4,000 suspended on 30-80 mesh firebrick.

The carrier gas was helium, and the column temperatures were in the range 145° to 155°. The preheater was maintained at 160° to 170°. The inlet pressures employed were 8.5 to 9.5 psig.

Monochloroethylene Carbonate. - Chlorine gas was passed into a flask containing 139 g. of freshly distilled ethylene carbonate. The reaction was carried out with ultraviolet light initiation, and a temperature of 63° to 70° was maintained. After 15 hours, 41 g. of chlorine was absorbed. Fractional distillation gave 56 g. of product (20%), b.p. 106-109° (10 mm.),  $n_D^{25}$  1.4496 (lit.<sup>2</sup> b.p. 106-107°, 10-11 mm.,  $n_D^{25}$  1.4530).

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<sup>1</sup> All melting and boiling points are uncorrected. The melting point determinations of the bicyclic and tetracyclic compounds were carried out in sealed capillaries. Infrared spectra were obtained with a Beckman Model IR - 4, or with a Perkin-Elmer Infracord Spectrophotometer. A Varian Associates DP-60 High Resolution Spectrometer was used for the nuclear magnetic resonance spectra; carbon tetrachloride was the solvent, and tetramethylsilane was the internal standard. Chemical shifts were obtained by the audio side-band technique.

<sup>2</sup> M.S. Newman and R.W. Alder, J. Am. Chem. Soc., **75**, 1264 (1953).

Vinylenes Carbonate. - Over a 7 hour period, a solution of 25.3 g. (0.25 mole) of triethylamine in 50 ml. of anhydrous ether was added dropwise to 30 g. (0.25 mole) of monochloroethylene carbonate in 100 ml. of anhydrous ether. The addition was carried out at reflux, and the mixture was heated for an additional 16 hours. The solution was filtered, and the solids were washed with three-100 ml. portions of ether. After removal of the solvent by distillation, the residue was distilled to give 14.8 g. (62%) of vinylenes carbonate, b.p.  $65^{\circ}$  (37 mm.),  $n_D^{25} 1.4203$  (lit.<sup>1</sup> b.p.  $73-74^{\circ}$ , 32 mm.,  $n_D^{25} 1.4190$ ).

Diels-Alder Addition of Vinylenes Carbonate to Cyclopentadiene. - A mixture of 58 g. (0.88 mole) of freshly distilled cyclopentadiene, 74 g. (0.87 mole) of vinylenes carbonate, and 60 g. of dry benzene was sealed in a combustion tube under nitrogen, and the solution was heated at  $175^{\circ}$  for 16 hours. The adduct was isolated by distillation, b.p.  $149-152^{\circ}$  (4 mm.). Recrystallization was effected from a mixture (1 : 1) of hexane and carbon tetrachloride. The product (41 g., 31%) melted at  $45^{\circ}$  (lit.<sup>2</sup> m.p.  $114.4-115^{\circ}$ ) indicating that the product was still impure. Further purification was not successful.

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1  
N.S. Newman and R.W. Addor, J. Am. Chem. Soc., **75**,  
1264 (1953).

2  
N.S. Newman and R.W. Addor, J. Am. Chem. Soc., **77**,  
379 (1955).

endo-cis-Bicyclo [2.2.1] hept-5-ene-2,3-diol. - The adduct of vinylene carbonate and cyclopentadiene (41 g., 0.27 mole) was heated at reflux for 3 hours with 150 ml. of 10% alcoholic potassium hydroxide. The product was extracted with two-150 ml. portions of ether. The ether solution was washed with two-150 ml. portions of water, and was dried over magnesium sulfate. After distillation of the solvent, 30.5 g. (91%) of a semi-solid was collected, b.p. 56-63° (0.8-1.1 mm.). The distilled product could not be crystallized. It gave a weakly positive test ( $\text{Br}_2/\text{CCl}_4$ ) for unsaturation. Attempts to hydrogenate this product were unsuccessful.

exo- and endo-3,4-Dibromobicyclo [3.2.1] octa-2,6-diene. -

To 420 ml. of dry *t*-butanol was added 20 g. of potassium. The excess *t*-butanol was removed by distillation, and the white cake of potassium *t*-butoxide was dried at 45° (0.5 mm.). To the resulting dry solid was added 250 ml. of olefin-free *n*-pentane which had previously been distilled from lithium aluminum hydride. This was followed by the addition of 230 g. (0.40 mole) of freshly distilled norbornadiene (b.p. 90°,  $n_D^{25}$  1.4677), while the temperature of the mixture was at 5°. Efficient stirring was maintained while 130 g. (0.51 mole) of bromoform was added dropwise over a period of two hours. Care was taken to see that the reaction temperature did not go above 5°. After the addition of the bromoform was completed, the mixture was stirred at room temperature for an additional 2 hours. The mix-

ture was poured onto 300 g. of ice, and then extracted with four-100 ml. portions of a mixture (1 : 1) of ether and *n*-pentane. The combined extract was washed with two-100 ml. portions of water, and dried over magnesium sulfate. After removal of the pentane, unreacted norbornadiene, and *n*-butanol by distillation, the product was collected at 83-85° (0.75 mm.) and 85-86° (0.75 mm.), (lit.<sup>1</sup> b.p. 77°, 0.95 mm.). Redistillation afforded 83 g. (61%) of 3,4-dibromobicyclo-[3.2.1] octa-2,6-diene, b.p. 85° (0.75 mm.). The infrared spectrum showed major bands at 3050(w), 2950(s), 1625(m), 1450(m), 1330(s), 1040(s), 855(m), 843(m), and 744(s) cm<sup>-1</sup>. This product also contained 2-6% of the tricyclic dibromide.<sup>2</sup>

3-Bromobicyclo [3.2.1] octa-2.6-diene. - Dry tetrahydrofuran was obtained after reflux over lithium aluminum hydride. A solution of 172 g. (0.65 mole) of the freshly distilled dibromocarbene adduct in 150 ml. of dry tetrahydrofuran was added dropwise to a suspension of 150 ml. of dry tetrahydrofuran and 7.41 g. (0.195 mole) of lithium aluminum hydride at ice-bath temperature. The addition required 2 hours, and the mixture was then stirred at room temperature for 1 hour and was heated at reflux for two hours. The excess lithium aluminum hydride was destroyed by the careful addition of 600 ml. of water, and the product was extracted with four-150 ml. portions of pentane. The combined extracts were washed with

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<sup>1</sup> W.R. Moore, W.R. Moser, and J.R. LaPrade, J. Org. Chem., **28**, 2700 (1963).

<sup>2</sup> Ibid.



two-150 ml. portions of water, two-100 ml. portions of saturated sodium bicarbonate solution, and finally with 100 ml. of saturated sodium chloride solution. The extract was dried and concentrated. The crude product was distilled, b.p.  $30-32^{\circ}$  (0.08 mm.). Redistillation gave 61 g. (51%) of pure 3-bromobicyclo [3.2.1] octa-2,6-diene, b.p.  $25^{\circ}$  (0.09 mm.),  $n_D^{25}$  1.5348 (lit.<sup>1</sup> 1.5336). Another fraction was distilled at  $66-77^{\circ}$  (0.2 mm.); it is possible that this is a dibromide resulting from the reduction of the tetrabromo dicarbene adduct. No further work was done on this latter fraction. The infrared spectrum of the vinyl bromide (pure liquid) showed major bands at 3120(s), 3000(s), 1655(s), 1350(s), 1053(s), and 837(s)  $\text{cm}^{-1}$ . N.m.r., Figure 1: 1.5-2.9 complex; quartets at 5.81 $\delta$  and 6.22 $\delta$ ; and, a singlet at 6.42 $\delta$ .

3,5,8-Tribromobicyclo [3.2.1] oct-2-ene. - A solution of 61 g. (0.33 mole) of 3-bromobicyclo [3.2.1] octa-2,6-diene in 150 ml. of anhydrous ethyl ether was cooled to  $-10^{\circ}$  by means of a Dry-Ice-carbon tetrachloride bath. To the above solution was added dropwise 63 g. (0.39 mole) of bromine (20% excess) over a period of 2½ hours. Sufficient ether was added to effect complete solution of the tribromide. The ether layer was washed with four-500 ml. portions of saturated sodium bisulfite solution, and then dried over anhydrous magnesium sulfate. After removal of

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<sup>1</sup>W.R. Moore, W.R. Moser, and J.E. LaPrade, J. Org. Chem., **28**, 2200 (1963).

of the solvent under reduced pressure, 108 g. (79.5%) of the white, crystalline tribromide was obtained, m.p. 97-98°.

Anal. Calcd. for  $C_8H_9Br_3$ : C, 27.85; H, 2.60; Br, 69.51. Found: C, 27.62; H, 2.60; Br, 69.39.

The infrared spectrum ( $CHCl_3$ ) showed major bands at 2960(m), 2930(m), 1640(s), 1450(s), 1318(s), and 978(s)  $cm^{-1}$ . N.m.r., Figure 2: 2.0-3.16  $\delta$  complex; 4.32  $\delta$  triplet; 4.4  $\delta$  singlet; and, at 6.13  $\delta$  a doublet.

Tetracyclo [3.3.0<sup>2,8</sup>.0<sup>4,6</sup>]octan-3-one. - A mixture of 100 ml. of water, 140 ml. of concentrated sulfuric acid, and 200 ml. of 95% ethanol was prepared and cooled to room temperature. To this solution was added 106 g. (0.31 mole) of 3,6,8-tribromobicyclo [3.2.1]oct-2-ene. While efficient stirring was maintained, the solution was heated at 50° for 24 hours. The reaction mixture was then poured onto 500 g. of ice, and was carefully neutralized with potassium hydroxide. The product was extracted with four 400 ml. portions of a mixture (1 : 1) of ethyl ether and pentane, and the combined extract was back-washed with two 400 ml. portions of water. After drying, distillation of the solvent gave 73.4 g. of a crude product whose infrared spectrum showed strong carbonyl absorption. The product was chromatographed on 1100 g. of acid-washed alumina (Merck), and 18.7 g. (51%) of crude ketone was ob-



tained by elution with 5% ethyl ether - 95% pentane.

The crude ketone was contaminated by bromides (alcoholic silver nitrate test), and was chromatographed once again on 400 g. of acid-washed alumina. Elution with 1 : 19 ethyl ether - pentane afforded 5.32 g. (14%) of ketone. Although gas chromatography (Polyglycol E-4,000, 150° and 5 psig.) showed one major peak present, an alcoholic silver nitrate test indicated that a bromide contaminant was still present. The ketone was then washed with 15 ml. of cold pentane, and the pentane layer was removed by decantation. The residue consisted of 4.93 g. (13%) of pure ketone, m.p. 63.5-67.5° with prior softening at 59.5°. The tetracyclic ketone was sublimed from anhydrous sodium sulfate at atmospheric pressure and 50°, m.p. 68-69°. The infrared spectrum ( $\text{CHCl}_3$ ) showed major bands at 2975(m), 2940(w), 2860(w), 1725(s), 1318(m), 1050(w), and 868(s)  $\text{cm}^{-1}$ . N.m.r., Figure 3: 1.3-2.6  $\delta$  complex. The ultraviolet spectrum shows absorption at  $\lambda_{\text{max}}^{\text{O}_2\text{H}_5\text{OH}} = 281\mu (\epsilon = 51)$ .

Anal. Calcd. for  $\text{C}_8\text{H}_8\text{O}$ : C, 79.97; H, 6.71. Found: C, 79.76; H, 6.93.

The 2,4-dinitrophenylhydrazone was prepared, and chromatographed on acid-washed alumina (Merck) with benzene as the eluent. The purified derivative was recrystallized several times from absolute ethanol, m.p. 225-226° dec.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{13}\text{N}_4$ : C, 56.00; H, 4.03; N, 18.66. Found: C, 56.06; H, 4.28; N, 18.46.

Tetracyclo [3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>] octan-3-ol. - To 8.0 ml. of absolute methanol was added 2.94 g. of tetracyclo-  
[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>] octan-3-one at 0°. After solution of the ketone was effected, 0.92 g. of sodium borohydride was slowly added. The reaction mixture was stirred at 0° for 30 minutes, and at room temperature for an additional 30 minutes. Water (75 ml.) was added dropwise, followed by an additional 75 ml. of water. The product was extracted with two-75 ml. portions of ethyl ether and three-75 ml. portions of pentane. The combined extract was dried over sodium sulfate, and the solvents were removed by distillation. Gas chromatography (Polyglycol E-4,000, 150° and 9 psig.) showed two peaks in a 40 : 60 ratio corresponding to the endo- and exo- epimers; 1.27 g. (43%) of crude product was obtained.

A portion of this material (1.06 g.) was chromatographed on 75 g. of acid-washed alumina. Fractions of 100 ml. were taken with 1 : 19 ethyl ether - pentane eluent. There was obtained in fractions 18 to 22, 0.252 g. of a solid material which was recrystallized from pentane, m.p. 52-54°. The infrared spectrum (CHCl<sub>3</sub>) of this material showed major bands at 3550(m), 3400(m), 2980(s), 2900(s), 2820(s), 1390(s), 1285(s), 1230(s), 1065(s), 1030(s), and 910(m) cm.<sup>-1</sup>.

Oxidation of a Mixture of endo- and exo-Tetracyclo-  
[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>] octan-3-ol. - To a mixture of 300 mg. of

chromic anhydride in 5.0 ml. dry pyridine at 0° was added 190 mg. of the alcohol mixture. After 6 hours of stirring at 0°, 100 ml. of water was added, and the product was extracted with two-50 ml. portions of ethyl ether and three-50 ml. portions of pentane. The combined extract was washed with 75 ml. of 10% hydrochloric acid and 75 ml. of 5% sodium bicarbonate solution. The extract was dried and concentrated to give 40.7 mg. (22%) of crude product. The infrared spectrum of this material was identical with that of tetracyclo [3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]octan-3-one. The 2,4-dinitrophenylhydrazone derivative of the recovered material decomposed at 224-225°. Gas chromatography showed a band with the same retention time as the original ketone, and admixture with an authentic sample of the ketone showed a single peak.

Attempted Hydrolysis of *endo*- and *exo*-3,4-Dibromobicyclo [3.2.1]octa-2,6-diene.— A mixture of 10 ml. of water, 14 ml. of concentrated sulfuric acid, and 20 ml. of 95% ethyl alcohol was prepared, and to it was added 10 g. of the dibromocarbene adduct of norbornadiene. The reaction mixture was heated at 45 - 50° for 48 hours, and was then poured onto 150 g. of ice. After neutralization with potassium hydroxide, the product was extracted with four-50 ml. portions of a 1 : 1 ethyl ether - pentane mixture. The infrared spectrum of the residue showed no car-

bonyl absorption; however, it did show weak hydroxyl absorption.

Attempted Base-Catalyzed Hydrolysis of 3-Bromobicyclo [3.2.1]octa-2,6-diene. - To 4.5 g. of the vinyl bromide was added 150 ml. of water and 3.35 g. of lithium carbonate. The suspension was heated at reflux for 4 days. Silver carbonate (7.4 g.) was added, and reflux was continued for 6 more days. The mixture was poured onto 100 ml. of water, and the product was extracted with five-50 ml. portions of hexane; the combined extract was then dried. Distillation of the solvent gave a residue which did not give a positive test with 2,4-dinitrophenylhydrazones. The starting material was recovered.

A mixture of 20 ml. of dimethyl sulfoxide, 0.75 g. of lithium carbonate, 20 ml. of water, and 1.0 g. of the vinyl bromide was heated at reflux for 22 hours. The solution was poured onto 100 ml. of water, and the products were extracted with four-25 ml. portions of ethyl ether. After drying, and distillation of the solvent, a residue, b.p.  $35^{\circ}$  (10 mm.) was obtained. The infrared spectrum of this material did not show carbonyl absorption. The 2,4-dinitrophenylhydrazone test was also negative; however, upon standing, a precipitate was slowly formed. This hydrolysis was attempted under the same conditions, but containing added silver carbonate. Again, the infrared spectrum of the residue showed no carbonyl absorption, and starting material was recovered.

In addition to showing no carbonyl absorption, the infrared spectrum of the residue was identical with that of the vinyl bromide. Purification of the residue afforded authentic starting material.

## BIBLIOGRAPHY

- Adler, E. and Reubke, R., Ber., 91, 1525 (1958).
- Adler, E. and Stein, G., Angew. Chem., 50, 510 (1937).
- Bergman, E., Abstracts, 142nd Meeting, American Chemical Society, Atlantic City, N.J., September 9-14, 1962.
- Bergman, E., Shell Chemical Company Publication P-1132.
- Cope, A.C., Oriser, J.W., and Peterson, P.E., J. Am. Chem. Soc., 82, 4299 (1960).
- Cope, A.C., Moon, S., and Peterson, P.E., J. Am. Chem. Soc., 84, 1928 (1962).
- Cristol, S.J. and Freeman, P.E., J. Am. Chem. Soc., 83, 4427 (1961).
- von Doering, W.E. and Hoffmann, A.E., J. Am. Chem. Soc., 76, 6162 (1954).
- Dolejack, R., Hamus, V., and Prinzbach, H., Angew. Chem. Int. Ed., 1, 598 (1962).
- Ghosez, L. and Laroche, P., Proc. Chem. Soc., March (1963).
- Hofmann, K., Orochena, S.F., Sax, S.R., and Jeffrey, C.A., J. Am. Chem. Soc., 81, 992 (1959).
- Jefford, C.W., Proc. Chem. Soc., February (1963).
- Kwart, H. and Vosburgh, W.G., J. Am. Chem. Soc., 76, 4072, (1954).
- Kwart, H. and Vosburgh, W.G., J. Am. Chem. Soc., 76, 5400, (1954).
- Moore, W.R., Moser, W.R., and LaPrade, J.E., J. Org. Chem., 28, 2200 (1963).
- Newman, M.S. and Addor, R.W., J. Am. Chem. Soc., 75, 1264, (1953).
- Newman, M.S. and Addor, R.W., J. Am. Chem. Soc., 77, 379, (1955).
- Nikon, A. and Lambert, J.L., J. Am. Chem. Soc., 84, 4605, (1962).

von Schleyer, P. and Nicholas, S., Abstracts, 140th Meeting, American Chemical Society, Chicago, September 3-8, 1961.

Skell, P.S. and Garner, A.Y., J. Am. Chem. Soc., 78, 3409 (1956).

Skell, P.S. and Garner, A.Y., J. Am. Chem. Soc., 78, 5430 (1956).

Skell, P.S. and Sandler, S.R., J. Am. Chem. Soc., 80, 2024 (1958).

Sonnenberg, J. and Winstein, S., J. Org. Chem., 27, 748 (1962).

Winstein, S. and Sonnenberg, J., J. Am. Chem. Soc., 83, 3235 (1961).

Winstein, S. and Sonnenberg, J., J. Am. Chem. Soc., 83, 3244 (1961).

Winstein, S., Sonnenberg, J., and DeVries, L., J. Am. Chem. Soc., 81, 6523 (1959).

Winstein, S., Sonnenberg, J., and DeVries, L., J. Am. Chem. Soc., 81, 6524 (1959).

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