

consistent with that of authentic *1,2-dichloro-2-methylpropane* (XII) b.p. 103–104°,  $n^{23}_D$  1.4344, prepared by photochlorination of *t*-butyl chloride. *1-Chloro-2-methylpropene* (XIII) was prepared by isomerization of XI by the method of Burgin, Hearne, and Rust<sup>32</sup> and had b.p. 68°,  $n^{23.5}_D$  1.4199 (lit.<sup>32</sup> b.p. 68.1°,  $n^{20}_D$  1.4221); its g.l.c. retention time was slightly shorter than that of XI and identical with that of a trace product of chlorination of isobutylene although the latter was never isolated. *1,2,3-Trichloropropane* (XIV), obtained from chlorination of allyl chloride followed by distillation, was identical with commercial material (Matheson Coleman and Bell). A commercial sample labeled “1,3-dichloropropene, high boiling” (Columbia Organic Chemicals) showed two major bands in the g.l.c. spectrum, each of which was collected by preparative g.l.c. and shown to be >99% pure by g.l.c. The first had  $n^{23.5}_D$  1.4676 (lit.<sup>33</sup>  $n^{25}_D$  1.4652 for XV) and both the infrared and n.m.r. spectra were consistent with those reported<sup>34,35</sup> for *cis*-1,3-dichloropropene (XV). The second had  $n^{23.5}_D$  1.4735 (lit.<sup>33</sup>  $n^{25}_D$  1.4712 for XVI) and both the infrared and n.m.r. spectra were consistent with those reported<sup>34,35</sup> for *trans*-1,3-dichloropropene (XVI). *3,3-Dichloropropene* (XVIII) was prepared by treatment of acrolein with phosphorus pentachloride<sup>36</sup> and had  $n^{23}_D$  1.4478 and b.p. 83–84° (lit.<sup>36</sup>  $n^{20}_D$  1.4510 and b.p. 83°). Commercial *2,3-dichloropropene* (XVII) (Matheson Coleman and Bell) had a retention time different

(31) J. M. Hersh and R. E. Nelson, *J. Am. Chem. Soc.*, **58**, 1631 (1936).

(32) J. Burgin, G. Hearne, and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

(33) L. F. Hatch and R. H. Perry, Jr., *J. Am. Chem. Soc.*, **71**, 3262 (1949).

(34) W. C. Wolfe, H. M. Doukas, and J. S. Ard, *ibid.*, **76**, 627 (1954).

(35) F. S. Mortimer, *J. Mol. Spectry.*, **3**, 335 (1959).

(36) L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, **70**, 3456 (1948).

from any of the chlorination products of allyl chloride.

**Quantitative Chlorinations.** The procedure was the same as described previously<sup>1b</sup> except that the constant temperature bath was maintained at  $-9 \pm 0.2^\circ$  and the reaction flask was fitted with a Dry Ice reflux condenser filled with Dry Ice. The butenes were introduced as gases and the amount used determined from volumetric calibration marks on the reaction flask; solvents were introduced by pipet. The g.l.c. analyses were performed with a Micro-Tek 2500R instrument equipped with 2-m. Perkin-Elmer “R” columns (polypropylene glycol) and a flame ionization detector. Injections were performed with a pressure-tight sampler (Micro-Tek Snap Sampler) for samples boiling below room temperature. Except for runs with allyl chloride, analyses were performed at 52°; the retention times in minutes at a helium flow rate of ca. 200 ml./min. were: I, 4; XIII, 5; XI, 6; VII, 6.25; IX, 8; II and VI, 8.5; X, 9.5; XII, 18; III, 21; IV, 24; and VIII, 28. For allyl chloride, analyses were performed at 92°; the retention times in minutes were: XVIII, 3.3; XVII, 5; XV, 5.7; XVI, 7.7; and XIV, 25. All areas were determined from the product of peak height and retention times. These areas were corrected to molar quantities by calibration factors determined from analysis of known mixtures; such factors were not determined for the minor substitution products from allyl chloride (XV and XVI); since the *cis-trans* pair II and VI could not be separated, the same calibration factor was assumed for each. The calibration factors were close to unity except for cases where compounds with different numbers of carbon atoms were compared. Results shown in Tables I–IX were obtained by this general procedure.

**Acknowledgment.** The author wishes to acknowledge the encouragement of and discussions with Dr. R. L. Hinman.

## The Stereochemistry of the Bicyclo[3.2.1]octane System. III.<sup>1,2</sup> The Addition of Dihalocarbene to Bicyclic Olefins

C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell<sup>3</sup>

*Contribution from the Chemistry Department, Temple University, Philadelphia, Pennsylvania 19122. Received November 25, 1964*

*Reaction of dihalocarbene with norbornene, 1-methylnorbornene, 2-methylnorbornene, and bicyclo[2.2.2]octene-2 furnished derivatives of bicyclo[3.2.1]octene-2 and bicyclo[3.2.2]nonene-2, respectively. Their structures were substantiated by nuclear magnetic resonance (n.m.r.) spectroscopy.*

(1) For part II see B. Waegell and C. W. Jefford, *Bull. soc. chim. France*, **844** (1964).

(2) Part of this work was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 33C.

(3) Visiting Lecturer for the Summer Session, 1964, on leave from the Institute de Chimie, Strasbourg, France.

### Introduction

We had reported earlier<sup>4</sup> that the reaction of dihalocarbenes with norbornene afforded direct entry to the bicyclo[3.2.1]octene-2 system.<sup>5,6</sup> Furthermore, we ex-

(4) C. W. Jefford, *Proc. Chem. Soc.*, **64** (1963).

(5) This fact has been subsequently corroborated by others: (a) L. Ghosez and P. Laroche, *ibid.*, **90** (1963); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (c) R. C. De Selms and C. M. Combs, *ibid.*, **28**, 2206 (1963); (d) E. Bergmann, *ibid.*, **28**, 2210 (1963).

(6) The course of addition of dihalocarbene to bicyclo[2.2.1]heptadiene is similar to the norbornene case: V. Franzen, *Rev. Chim. (Bucharest)*, **7**, 859 (1962). See also ref. 5b.

ploited this finding to prepare convenient quantities of bicyclo[3.2.1]octanone-3 (I) which was needed for a study of the validity of the reflex effect.<sup>7,8</sup> We prepared bromo derivatives of I and showed that a reflex effect operates in bicyclo[3.2.1]octanone-3 in an opposite sense to that experienced in 3,3,5,5-tetramethylcyclohexanone.<sup>1,9</sup>

It is well known that dihalocarbene and a strained monocyclic olefin can form a cyclopropane adduct which undergoes rearrangement to the ring-expanded allylic halide.<sup>10,11</sup>

As previously noted, this reaction becomes particularly interesting when a bicyclic olefin is chosen, as then a precisely substituted new bicyclic system can be obtained from a simple precursor.

The present study is concerned with the generality and stereochemistry of the over-all reaction of dihalocarbene with norbornene, 1-methylnorbornene, 2-methylnorbornene, and bicyclo[2.2.2]octene-2 together with an analysis of the n.m.r. spectra of the products of reaction.

## Results

**Norbornene and Dihalocarbene.** The interaction of a twofold excess of dibromocarbene with norbornene in pentane at room temperature afforded a single 1:1 adduct (II) in yields which varied from 25 to 40%. The structure of II was assigned on the basis of spectral and chemical evidence.<sup>12</sup>

The infrared spectrum of II indicated a double bond (maximum at 1625 cm.<sup>-1</sup>).

The n.m.r. spectrum of II revealed the presence of four kinds of proton: vinyl (1H), allylic (1H), bridgehead (2H), and methylene (6H). Substitution of  $J_{\text{H}_\text{BHC}}$  (see Table I) in the Karplus equation<sup>13</sup> predicted the same dihedral angle for the vinyl and bridgehead protons as is found from a Dreiding model,<sup>14</sup> namely, 22°. However, a similar calculation for  $J_{\text{H}_\text{AHD}}$  did not enable an unambiguous prediction of the dihedral angle for the allylic and bridgehead protons to be made. Fortunately, n.m.r. data on the isomeric 1-methyl-2,3-benzbicyclo[3.2.1]-4-octanols III and IV were available for comparison<sup>15</sup> (see Table I) and indicated that the allylic proton in II had the *endo* configuration.<sup>16,17</sup> This indication was substantiated by the hydrolysis of 3,4-dibromobicyclo[3.2.1]octene-2 (II) with silver nitrate in aqueous acetone to *exo*-3-bromo-4-hydroxybicyclo[3.2.1]octene-2 (V). Oxidation of V gave 3-bromobicyclo[3.2.1]oct-2-en-3-one (VII). Sodium borohydride reduction of VII afforded a mixture of the epimeric octenols which were separated by column chromatography. The major product (assumed to be the *endo* octenol VI) exhibited a doublet

at 263 c.p.s. for the allylic proton ( $J_{\text{H}_\text{A}/\text{H}_\text{D}} = 4.8$  c.p.s.). The other isomer V showed a doublet at 225 c.p.s. ( $J_{\text{H}_\text{A}/\text{H}_\text{D}} = 2.8$  c.p.s.) (see Table I).

The reaction of dichlorocarbene and norbornene gave *exo*-3,4-dichlorobicyclo[3.2.1]octene-2 (VIII) usually in about 10% yield. Its structure was inferred by analogy. N.m.r. spectral data of the allylic and vinyl protons of VIII are recorded in Table I.

**Bicyclo[2.2.2]octene-2 and Dibromocarbene.** The addition of a twofold excess of dibromocarbene to bicyclo[2.2.2]octene-2 afforded two isomeric products IX and X in 2.57 and 6.58% yields, respectively. The products were easily separated by fractional distillation *in vacuo*. Thin layer chromatography showed them to be chiefly single compounds. Analysis showed them to have the empirical formula C<sub>9</sub>H<sub>12</sub>Br<sub>2</sub>.

The structures of IX and X were assigned on the basis of their infrared and n.m.r. spectra as well as chemical evidence. X possessed a band at 1625 cm.<sup>-1</sup>, whereas IX did not.

The n.m.r. spectrum of X shows four kinds of proton: vinyl (1H), allylic (1H), bridgehead (2H), and methylene (8H), whereas the n.m.r. spectrum of IX shows no vinyl or allylic resonances and only three kinds of proton: cyclopropyl bridgehead, bridgehead, and methylene. IX cannot be isomerized to X on heating. Accordingly X is 3,4-dibromobicyclo[3.2.2]-nonene-2. IX was shown to be *exo*-3,3-dibromotricyclo[4.2.1.0<sup>2,4</sup>]-nonane (identical with a sample prepared from bicyclo[3.2.1]octene-2).

Treatment of X with aqueous silver nitrate resulted in an immediate precipitate of silver bromide with formation of 3-bromo-4-hydroxybicyclo[3.2.2]nonene-3 (XI). N.m.r. data of XI are listed in Table I.

Further proof for the structure of X was provided by its reduction with lithium aluminum hydride to 3-bromobicyclo[3.2.2]nonene-2 (XII), followed by the hydrolysis of XII to bicyclo[3.2.2]nonanone-3 (XIII).

**1-Methylnorbornene and Dihalocarbene.** The results of the dihalocarbene addition to 1-methylnorbornene are summarized in Figure 1. The isomeric composition was remarkably constant and the percentages recorded in Figure 1 are reproducible.

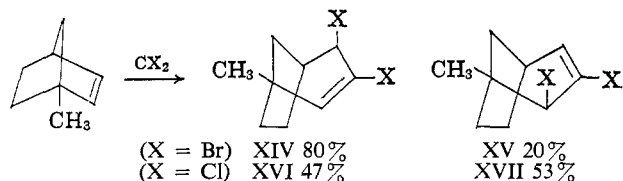


Figure 1.

Both the addition of dibromo- and dichlorocarbene to 1-methylnorbornene afforded products of empirical formula C<sub>9</sub>H<sub>12</sub>X<sub>2</sub> in yields between 25 and 40%. The product was shown to consist of two components by t.l.c. Moreover, the n.m.r. spectrum showed two distinct sets of vinyl and allylic signals (see Table II), the separate integration of which afforded the isomeric composition. The products were *exo*-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 (XIV), *exo*-1-methyl-2,3-dibromobicyclo[3.2.1]octene-3 (XV), and their dichloro analogs XVI and XVII.

The allylic halogen atom in all cases is assumed to have the *exo* configuration on the basis of the results from the norbornene-dihalocarbene reaction.<sup>17</sup> The

(7) C. Sandris and G. Ourisson, *Bull. soc. chim. France*, 1524 (1958).

(8) B. Waegell and G. Ourisson, *ibid.*, 496, 503 (1963).

(9) C. W. Jefford and B. Waegell, *Tetrahedron Letters*, No. 28, 1981 (1963).

(10) W. Kirmse, *Angew. Chem.*, 73, 161 (1961).

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

(12) Lithium aluminum hydride reduction of II followed by acid hydrolysis gave bicyclo[3.2.1]octanone-3 (ref. 1 and 4).

(13) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); *J. Am. Chem. Soc.*, 85, 2870 (1963).

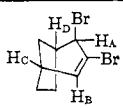
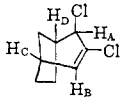
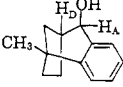
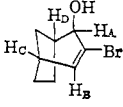
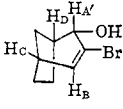
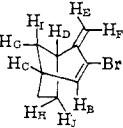
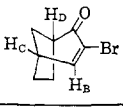
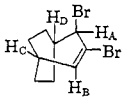
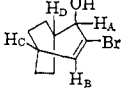
(14) W. Büchi, Glasapparate Fabrik, Flawil, Switzerland.

(15) W. Herz and G. Caple, *J. Am. Chem. Soc.*, 84, 3517 (1962).

(16) The ethane bridge side of the molecule is designated *endo*.

(17) The *exo* configurations of II, V, and XIV have been proved by double resonance experiments (C. W. Jefford, B. Waegell, and K. Ramey, *J. Am. Chem. Soc.*, 87, 2191 (1965)).

**Table I.** Chemical Shifts and Coupling Constants of Vinyl and Allylic Protons<sup>a</sup> of Bicyclo[3.2.1]octene and Bicyclo[3.2.2]nonene Derivatives

Compd.	Solvent	Signal of proton, c.p.s.	
		H <sub>B</sub>	H <sub>A</sub> or H <sub>A'</sub>
II 	CCl <sub>4</sub>	Doublet at 373, $J_{H_B H_C} = 7.0$ , $^4J = 1.00$	Doublet at 264, $J_{H_A H_D} = 2.8$ , $^4J = 0.6$
VIII 	CCl <sub>4</sub>	Doublet at 359, $J_{H_B H_C} = 7.0$ , further finely split	Doublet at 243, $J_{H_A H_D} = 2.8$ , further finely split
III <sup>b</sup> 	CDCl <sub>3</sub>		Doublet at 253, $J_{H_A H_D} = 2.8$
IV <sup>b</sup> <i>endo</i> epimer of III	CDCl <sub>3</sub>		Doublet at 297, $J_{H_A H_D} = 5.0$
V 	CCl <sub>4</sub>	Doublet at 377, $J_{H_B H_C} = 7.0$	Doublet at 225, $J_{H_A H_D} = 2.8$
VI 	CCl <sub>4</sub>	Doublet at 374, $J_{H_B H_C} = 7.0$	Doublet at 263, $J_{H_A' H_D} = 4.8$
		H <sub>B</sub>	H <sub>E</sub> and H <sub>F</sub>
XX 	CDCl <sub>3</sub>	Doublet at 391, $J_{H_B H_C} = 7.0$	Two singlets at 293 and 302
VII 	CCl <sub>4</sub>	Doublet at 451, $J_{H_B H_C} = 7.3$ , $^4J = 1.4$	
			H <sub>A</sub>
X 	CDCl <sub>3</sub>	Doublet at 384, $J_{H_B H_C} = 9.5$	Doublet at 300, $J_{H_A H_D} = 5.8$ , further finely split
XI 	CCl <sub>4</sub>	Doublet at 383, $J_{H_B H_C} = 9.5$	Doublet at 253, $J_{H_A H_D} = 4.0$ , further finely split

<sup>a</sup> Spectra were determined at 60 Mc. <sup>b</sup> Data were obtained from ref. 15.

assumption is corroborated by the size of the coupling constants of the allylic protons and the position of their chemical shifts (*cf.* Tables I and II).

Both pairs of binary mixtures (XIV and XV; XVI and XVII) proved difficult to separate on vapor phase chromatography, as they decomposed easily. Low-temperature (90–100°) thermolysis afforded equimolar amounts of *m*-halotoluene and ethylene. However, *exo*-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 (XIV) was obtained pure by fractional distillation of the mixture of products (XIV and XV).

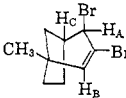
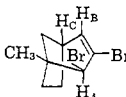
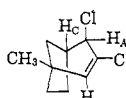
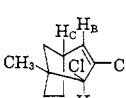
Additional proof for structure XIV was provided by its reduction with lithium aluminum hydride, followed by hydrolysis to a single product, 1-methylbicyclo[3.2.1]octanone-3 (XVIII).

**2-Methylnorbornene and Dibromocarbene.** The interaction of a twofold excess of dibromocarbene and 2-methylnorbornene afforded two products, both of

which polymerized on standing or heating. The more labile compound (XIX) appeared to be a 1:1 adduct of 2-methylnorbornene and dibromocarbene. XIX decomposed easily to a product of empirical formula C<sub>9</sub>H<sub>11</sub>Br. Reaction must have involved the addition of an equimolar amount of dibromocarbene and the elimination of an equimolar amount of hydrogen bromide. The structure of the C<sub>9</sub>H<sub>11</sub>Br product, 3-bromo-4-methylenebicyclo[3.2.1]octene-2 (XX), was assigned from a consideration of its infrared, ultraviolet, and n.m.r. spectra.

The n.m.r. spectrum revealed that six kinds of proton were present: three nonequivalent vinyl protons, two nonequivalent bridgehead protons, and six methylene protons. The doublet centered at 391 c.p.s. arises from the vinyl proton H<sub>B</sub>. The singlets at 293 and 302 c.p.s. are due to the geminal protons H<sub>E</sub> and H<sub>F</sub> with little or no coupling between them (Table

**Table II.** Chemical Shifts and Coupling Constants of Vinyl, Allylic, and Methyl Protons<sup>a</sup> of 1-Methylbicyclo[3.2.1]octene Derivatives<sup>b</sup>

	Compd.	Signal of proton, c.p.s.		
		Methyl group	H <sub>B</sub>	H <sub>A</sub> or H <sub>A'</sub>
XIV		74	Doublet at 365, <sup>4</sup> J = 1.4	Doublet at 268, J <sub>H<sub>A</sub>H<sub>C</sub></sub> = 2.8, <sup>4</sup> J = 0.4
XV		82	Doublet at 376, J <sub>H<sub>B</sub>H<sub>C</sub></sub> = 7.0	Singlet at 265
XVI		74	Doublet at 352, <sup>4</sup> J = 1.3	Doublet at 249, J <sub>H<sub>A</sub>H<sub>C</sub></sub> = 2.8
XVII		79	Doublet at 365, J <sub>H<sub>B</sub>H<sub>C</sub></sub> = 7.0	Singlet at 243

<sup>a</sup> Spectra were determined at 60 Mc. <sup>b</sup> All measurements were taken in CCl<sub>4</sub> solvent.

I). Comparison with the 100-Mc. spectrum of XX shows that the spacing between them is field dependent. The triplet at 185 c.p.s. may be ascribed to the bridgehead proton H<sub>D</sub> which couples only with H<sub>G</sub> and H<sub>H</sub> ( $J_{H_D H_G} = J_{H_D H_H} = \sim 5$  c.p.s.). The dihedral angles between H<sub>D</sub> and the other two protons H<sub>I</sub> (on the methylene bridge) and H<sub>J</sub> (on the ethane bridge) are both nearly 90° and therefore little or no coupling is expected. The other bridgehead proton H<sub>C</sub> shows up at 157 c.p.s. as a broad signal due to additional coupling with the vinyl proton H<sub>B</sub>.

The infrared spectrum of XX showed significant maxima at 845, 890, 1450, 1585, 1625, 1780, 3038, and 3095 cm.<sup>-1</sup>. The two maxima at 1585 and 1625 cm.<sup>-1</sup> may be ascribed to the C=C stretching of a conjugated diene. The maxima at 890 and 1450 cm.<sup>-1</sup> are characteristic of the out-of-plane and in-plane CH deformations, respectively, of a =CH<sub>2</sub> group. The maxima at 845 and 3038 cm.<sup>-1</sup> are consistent with the CH out-of-plane deformation and the CH stretching vibration, respectively, of the >C=C<<sub>H</sub> grouping.<sup>18</sup>

The ultraviolet spectrum showed a single maximum at 242 mμ (ε 20,000) which is characteristic of a conjugated diene system.<sup>19</sup>

### Discussion

The main reaction sequences are adumbrated in Figures 1 and 2. The significant feature is the conversion of a common bicyclic olefin to a hitherto less accessible higher homolog in a stereospecific manner.

*The Addition Process and Rearrangement.* It is clear that the initial product of the interaction of dihalocarbene and bicyclic olefin is a cyclopropane structure. Moreover, the cyclopropane adduct is best formulated as *exo*.<sup>5b,c,20</sup> For example, the adduct from norbornene (XXI) possesses considerable

strain: angle strain due to the presence of the cyclopropane ring, severe flagpole interactions due to van der Waal's repulsion between hydrogen and halogen

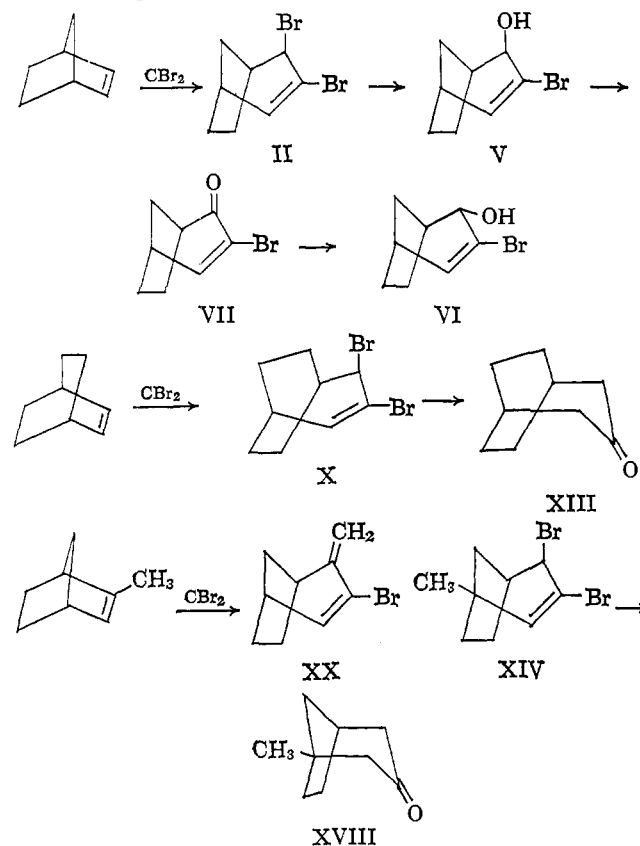


Figure 2.

atoms, and torsional strain associated with the regular boat conformation.<sup>21</sup> This strain can be alleviated by the formation of the postulated intimate ion pair XXII.<sup>22</sup> Migration of the halide ion to C-2 or C-4

(21) The ethane bridge prevents the adoption of the twist boat conformation and accordingly XXI probably contains at least 7.5 kcal./mole of strain due to the eclipsed boat.

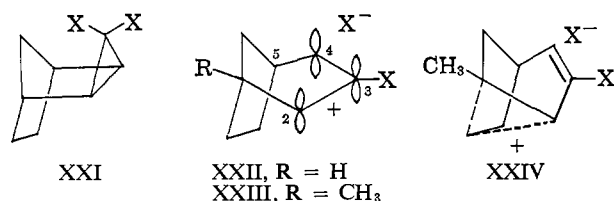
(22) The cation of XXII may be regarded as a rigid homocyclopropenyl ion; cf. E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962).

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 3.

(19) C. N. R. Rao, "Ultra-violet and Visible Spectroscopy. Chemical Applications," Butterworth and Co. (Publishers) Ltd., London, 1961, Chapter 4.

(20) R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964).

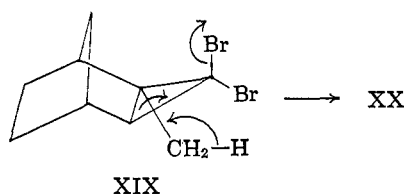
annihilates the ion pair and affords the product. The formation of only the *exo* product indicates that the



halide ion is situated over the face of the cyclohexenyl rather than the cycloheptenyl cation moiety.

However, when an unsymmetrical bicyclic olefin is used in the carbene addition, e.g., 1-methyl- and 2-methylnorbornene, then there may be more than one outcome of the rearrangement of the initial cyclopropane adduct if it occurs through the intermediacy of an ion pair such as XXII. It is remarkable that the addition of dibromo- and dichlorocarbene to 1-methylnorbornene yield two *exo* isomers and in quite different ratios (see Figure 1). This evidence strongly supports the idea of a common ionic intermediate, namely XXIII, and by extension, XXII. In the absence of any special factor the halide ion on the cyclohexenyl face should have an equal chance of migrating to C-2 or C-4. However, the difference in nucleophilicity and size between chloride and bromide ions constitutes such a special factor, the influence of which has clearly determined the observed product composition. It may be conjectured that C-2 is more electrophilic than C-4 due to the stabilizing effect of the C-1 methyl group (XXIV)<sup>23</sup> and thus will prefer chloride over bromide ion; and that the C-4 position can accommodate the bulky bromide ion better than the C-2 site.

The primary adduct formed from dibromocarbene and 2-methylnorbornene may be best written as the *exo* formulation XIX. However, rearrangement and elimination of hydrogen bromide in XIX probably occur simultaneously as there is no evidence of just a rearranged product.<sup>24</sup>



Because of the symmetry of bicyclo[2.2.2]octene-2, its interaction with dibromocarbene should furnish only one cyclopropane adduct (IX<sub>A</sub>). The production of IX together with its isomer X on thermal work-up indicates that IX is more stable than the cyclopropane adduct of dibromocarbene and bicyclo[2.2.2]octene-2. This is not unexpected in view of the smaller strain associated with bicyclo[3.2.1]octene-2 than with bicyclo-

(23) Alkyl substitution at C-1 certainly should encourage the migration of the ethane bridge to C-2. A singular example of such a rearrangement occurs during the peracetic acid oxidation of  $\alpha$ -patchoulene; G. Büchi, W. D. Macleod, Jr., and J. P. O., *J. Am. Chem. Soc.*, **86**, 4438 (1964).

(24) The addition of dihalocarbene with concomitant elimination of hydrogen halide usually occurs at the demand of some special driving force, such as aromatization. For example, cyclopentadiene and dichlorocarbene yield chlorobenzene: A. P. ter Borg and A. F. Bickel, *Rec. trav. chim.*, **80**, 1217 (1961). In the present case the achievement of the coplanar conjugated diene constitutes such a stabilizing factor.

[2.2.2]octene-2.<sup>25</sup> However, IX does possess severe *flagpole* interactions. Heat causes IX<sub>A</sub> to rearrange to its ring enlarged isomer (X), presumably through a state similar to the ion pair XXII already described.

It can be seen from Tables I and II that the chemical shifts and coupling constants are consistent with the related structures. The most interesting feature of several of the compounds is the fact that the signals of the vinyl and allylic protons possess additional fine structure.

For example, the vinyl and allylic protons in 3,4-dibromobicyclo[3.2.1]octene-2 (II) and its 1-methyl homolog XIV exhibit long-range coupling.<sup>26,27</sup> However, the fact that the <sup>4</sup>J values of the vinyl and allylic proton fine splitting are 1.00 and 0.60 c.p.s. for II and 1.4 and 0.40 c.p.s. for XIV is a striking revelation that the vinyl and allylic protons are *not* mutually coupled, but are coupled to some other protons.<sup>28</sup> This fact is corroborated by the observed fine splitting (<sup>4</sup>J = 1.4 c.p.s.) of the vinyl resonance in 3-bromobicyclo[3.2.1]oct-2-en-4-one (VII).

In the case of 3,4-dibromo- (X) and 3-bromo-4-hydroxybicyclo[3.2.2]nonene-2 (XI) long-range coupling causes the allylic proton, but *not* the vinyl proton, resonances to exhibit additional multiplicity.

## Experimental

**Spectral Determinations.** N.m.r. spectra were determined at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.) at normal operating temperature (ca. 25–30°). All compounds were investigated as approximately 10% solutions in reagent carbon tetrachloride or deuteriochloroform. Chemical shifts were measured in cycles per second (c.p.s.) from tetramethylsilane (which was used as an internal standard) and are considered accurate to  $\pm 1.0$  c.p.s. Coupling constants (*J*) are also given in c.p.s. and are considered accurate to  $\pm 0.10$  c.p.s. They were obtained from a first-order analysis of fine structure. Details of methyl, vinyl, and allylic protons of the compounds under study are listed in Tables I and II. Other pertinent n.m.r. spectral data are recorded below.

Infrared absorption spectra were determined either on a Perkin-Elmer Model 137-B Infracord spectrometer (NaCl prism) or Beckman IR-9 spectrometer (KBr and grating optics). Ultraviolet spectra were determined on a Beckman DK-2 spectrophotometer. Mass spectra were determined on a Bendix time-of-flight mass spectrometer. Microanalyses were performed by G. Robertson, Florham Park, N. J.

**Preparation of Bicyclic Olefins.** Conventional methods were used to prepare samples of norbornene<sup>29</sup> and bicyclo[2.2.2]octene-2.<sup>30</sup>

**1-Methyl- and 2-Methylnorbornene.** The method of preparation parallels that of preparing norbornene.

(25) IX probably arises from bicyclo[3.2.1]octene-2 present as a small impurity (~4%) in bicyclo[2.2.2]octene-2. The two olefins are differently strained as they possess cyclohexene moieties fixed in half-chair and boat conformations, respectively.

(26) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(27) E. W. Garbisch, *Chem. Ind. (London)*, 1715 (1964).

(28) Double resonance experiments of II and XIV show that the methylene bridge protons are involved. See ref. 17.

(29) J. Meinwald and N. J. Hudak, *Org. Syn.*, **37**, 65 (1957).

(30) N. A. LeBel, J. E. Huber, and L. H. Zalkow, *J. Am. Chem. Soc.*, **84**, 2226 (1962).

In place of cyclopentadiene dimer, commercially available, methylcyclopentadiene dimer (Enjay Co., Plainfield, N. J.)<sup>31</sup> was used. As the procedure has been reported previously only in outline,<sup>32</sup> full details of a typical reaction are described here. Methylcyclopentadiene dimer (340.0 g.) and sodium carbonate (10.0 g.) were placed in a bomb (1400-ml. capacity). The bomb was charged with ethylene to a pressure of 900 p.s.i. and heated for 7 hr. at 190°. On cooling, the contents of the bomb were filtered and distilled; the portion which distilled between 100 and 113° was collected. Redistillation was effected through a bubble cap column (75 cm. high and 2.6 cm. wide) containing 14 platforms. Fractions of b.p. 104–105° and 118–119° consisted of 1-methyl- and 2-methylnorbornene, respectively. The identities of the two isomers were corroborated by their n.m.r. spectra. Total yields were 80.0 g. of 1-methyl- and 200.0 g. of 2-methylnorbornene of 99.5 and 98.2% purity, respectively, the impurity in each case being the other isomer.

*General Procedure of Dihalocarbene Addition to Bicyclic Olefins.* Usually, dibromo- or dichlorocarbene was generated by the interaction of potassium *t*-butoxide and bromoform or chloroform in a pentane solution of the olefin according to Doering and Hoffmann's method.<sup>33</sup> Reactions were conducted under an atmosphere of dry nitrogen and at 0°. All final distillations were performed on a Nester-Faust spinning band still.<sup>34</sup> The products in all cases were monitored by thin layer chromatography (t.l.c.) and vapor phase chromatography (v.p.c.). T.l.c. was carried out on silica gel (Merck, according to Stahl) supported on a microscope slide. Elution was with 5 or 10% ethyl acetate in cyclohexane and development with a 50% aqueous sulfuric acid spray followed by heating on a hot plate.

*Interaction of Dibromocarbene and Norbornene, exo-3,4-Dibromobicyclo[3.2.1]octene-2 (II).* A two-fold excess of dibromocarbene was allowed to react with freshly distilled norbornene (29.2 g., 0.3 mole). The oil obtained on work-up was distilled *in vacuo* to give 20.0 g. of product (25% yield), b.p. 124° at 3 mm. Fractional distillation gave the pure compound, b.p. 104° at 1 mm. Yields in different experiments varied between 25 and 32%. The infrared absorption spectrum of the neat oil showed a band at 1625 cm.<sup>-1</sup>. T.l.c. indicated the presence of one isomer only. The n.m.r. spectrum of II showed four kinds of proton: methylene resonance at 100, 115, 125, and 136 c.p.s. (6H); a broad bridgehead signal at 160 c.p.s. (2H); and allylic (1H) and vinyl (1H) signals appeared at 264 and 373 c.p.s.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>Br<sub>2</sub>: C, 36.12; H, 3.79; Br, 60.10. Found: C, 36.17; H, 3.75; Br, 60.39.

*exo-3-Bromo-4-hydroxybicyclo[3.2.1]octene-2 (V).* *exo-3,4-Dibromobicyclo[3.2.1]octene-2 (II)* (17.0 g., 0.64 mole) in 50% aqueous acetone (250 ml.) was mixed with a solution of silver nitrate (11.9 g., 0.69 mole) in distilled water (22 ml.). An instantaneous precipitate of silver bromide formed. The mixture was heated under

reflux for 2 hr. The precipitate was removed by filtration and the filtrate was extracted with ether. The combined ether layers were dried over anhydrous magnesium sulfate, filtered, and evaporated on the steam bath. A colorless solid was obtained which was sublimed to give 8.28 g. of product (V, 64.0% yield), m.p. 72–73°. N.m.r. spectroscopy revealed only the presence of the *exo* isomer. There were five kinds of proton: methylene, a broad area at 108 and a sharper signal at 120 (6H); a broad bridgehead resonance at 154 (2H); a hydroxylic proton at 193 (variable in position) (1H); allylic at 225 (1H); and vinyl at 377 c.p.s. (1H).

*Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>BrO: C, 47.30; H, 5.46; Br, 39.45. Found: C, 47.45; H, 5.43; Br, 39.25.

*3-Bromobicyclo[3.2.1]oct-2-en-4-one (VII).* A solution of sodium dichromate (5.0 g., 0.017 mole), concentrated sulfuric acid (2.8 ml.), and distilled water (35 ml.) was stirred in a three-neck flask fitted with a thermometer and reflux condenser.<sup>35</sup> To this solution *exo-3-bromo-4-hydroxybicyclo[3.2.1]octene-2 (V)*, 5.5 g., 0.027 mole) was added in portions over 3 hr. The resulting solution was extracted with five 40-ml. portions of ether. The combined extracts were washed with dilute sodium bicarbonate solution and dried over anhydrous sodium sulfate. Filtration and removal of the ether left an oil (4.3 g.), b.p. 96–98° at 0.8 mm. The infrared absorption spectrum of the neat oil showed maxima at 1590 (medium), 1680 (strong), and 1730 cm.<sup>-1</sup> (medium), characteristic of an  $\alpha,\beta$ -unsaturated ketone (no -OH present). The ketone (VII) was characterized through its 2,4-dinitrophenylhydrazone derivative, m.p. 189°. The n.m.r. spectrum of V showed three kinds of proton: a methylene multiplex massif at 113 c.p.s. (6H), a merged triplet and broad peak at 182 c.p.s. due to bridgehead protons (2H), and a vinyl resonance at 451 c.p.s. (1H).

*Anal.* Calcd. for C<sub>14</sub>H<sub>13</sub>BrN<sub>4</sub>O<sub>4</sub>: C, 44.11; H, 3.44; Br, 20.96; N, 14.70. Found: C, 44.32; H, 3.59; Br, 20.39; N, 14.47.

*endo-3-Bromo-4-hydroxybicyclo[3.2.1]octene-2 (VI).* To a stirred solution of 3-bromobicyclo[3.2.1]oct-2-en-4-one (VII, 3.3 g., 0.17 mole) in isopropyl alcohol (50 ml.) was added a solution of sodium borohydride (1.6 g., 0.044 mole) in isopropyl alcohol (150 ml.). The reaction mixture was stirred for 2 days. The solution was evaporated and the residual oil was extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and then evaporated. The oily residue was sublimed to give a low-melting solid. N.m.r. spectroscopy indicated that it consisted of mainly the *endo* alcohol VI (75%), the minor component being the *exo* isomer V (25%). Yields were usually 40–50%, but variable. Purification was effected by column chromatography over silica to give a colorless solid m.p. ca. 35°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>BrO: C, 47.30; H, 5.46; Br, 39.45. Found: C, 47.14; H, 5.34; Br, 39.75.

*exo-3,4-Dichlorobicyclo[3.2.1]octene-2 (VIII).* Two procedures were followed: Doering's method<sup>33</sup> and the method of Parham and Schweizer.<sup>36</sup> Yields by

(31) We thank the Enjay Co. for a gift of this material.

(32) P. von R. Schleyer, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956, p. 20-O.

(33) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(34) Column height 61 cm., bore 8 mm., 28 plates.

(35) W. F. Bruce, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 139.

(36) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

both methods were usually low and never greater than 10%. The crude oil obtained on work-up usually contained much unchanged norbornene. A typical reaction making use of Parham's procedure for the generation of dichlorocarbene is as follows. A mixture of freshly distilled ethyl trichloroacetate (192.7 g., 1.0 mole) and norbornene (46.32 g., 0.5 mole) in dry, olefin-free pentane was stirred at room temperature. Under an atmosphere of nitrogen, sodium methoxide (55.0 g., 1.0 mole) was slowly added to the mixture. After the addition, stirring was continued at room temperature for 15 hr. The mixture was then shaken with water and extracted with pentane. The pentane solution was dried with magnesium sulfate, filtered, and distilled. The crude oil was distilled at 54–58° at 0.5 mm. affording 26.5 g. of distillate. The distillate on preparative vapor phase chromatography (Carbowax column at 150°) was shown to consist of unchanged starting materials and a single product in ca. 25% yield. Submission of this sample to n.m.r. spectroscopy showed it to be the *exo* isomer VIII.

*Interaction of Dibromocarbene and Bicyclo[2.2.2]octene-2.* 3,3-Dibromotricyclo[4.2.1.0<sup>2,4</sup>]nonane (IX). Dibromocarbene (0.5 mole) was allowed to interact with bicyclo[2.2.2]octene-2 (27.0 g., 0.25 mole) in pentane. Work-up gave an oil which on fractional distillation gave two distinct fractions, one of b.p. 84–88° at 1 mm. (1.8 g., 2.57% yield) and a second of b.p. 92–93° at 1 mm. (4.6 g., 6.58% yield). The preliminary distillation products were bicyclo[2.2.2]octene-2 and bromoform.

The low-boiling fraction (b.p. 84–88°) was mainly a single substance (as shown by t.l.c.). Traces of impurity were removed by chromatography over silica. The purified substance IX showed no absorption in the 1625-cm.<sup>-1</sup> region of the infrared spectrum and the fact that the n.m.r. spectrum was featureless beyond 265 c.p.s. indicated the absence of vinyl and allylic protons. Signals showed at 60 (broad) due to methylene protons (2H); an undoubted methylene massif at 100 and two broad signals at 128 and 142 c.p.s., due to cyclopropyl bridgehead and methylene protons (8H); and a broad peak at 156 c.p.s. due to bridgehead protons (2H). IX was also prepared in 40% yield by the addition of dibromocarbene to bicyclo[3.2.1]octene-2.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>Br<sub>2</sub>: C, 38.60; H, 4.29; Br, 57.20. Found: C, 39.08; H, 4.40; Br, 57.15.

*3,4-Dibromobicyclo[3.2.2]nonene-2 (X).* The high-boiling fraction (b.p. 92–93°) X was shown to be a single substance by t.l.c., showed a maximum at 1625 cm.<sup>-1</sup> in the infrared (double bond present) and moreover its n.m.r. spectrum (in CDCl<sub>3</sub>) is characteristic of 3,4-dibromobicyclo[3.2.2]nonene-2 (X). There were four kinds of proton: two broad areas centered at 105 c.p.s. due to methylene protons (8H), a bridgehead proton resonance at 140 c.p.s. (broad, 2H), the allylic proton showed at 300, and the vinyl at 384 c.p.s.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>Br<sub>2</sub>: C, 38.60; H, 4.29; Br, 57.20. Found: C, 39.38; H, 4.42; Br, 56.42.

It proved difficult to obtain a better elemental analysis for X. Attempted chromatographic purification of X over silica or neutral alumina resulted in decomposition.

*3-Bromo-4-hydroxybicyclo[3.2.2]nonene-2 (XI).* To a solution of 3,4-dibromobicyclo[3.2.2]nonene-2 (X, 1.0 g.) in 50% aqueous acetone (60 ml.) a solution of

silver nitrate (1.0 g. in 10 ml. of water) was added. Silver bromide was immediately deposited. The mixture was heated under reflux overnight and then extracted with ether. The ether was dried over anhydrous magnesium sulfate and evaporated. The residual colorless solid (0.69 g., 95.5% yield) was recrystallized from petroleum ether (b.p. 60–70°), m.p. 98–99.5°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>BrO: C, 49.77; H, 5.99; Br, 36.86. Found: C, 49.70; H, 6.02; Br, 36.58.

*3-Bromobicyclo[3.2.2]nonene-2 (XII).* A solution of 3,4-dibromobicyclo[3.2.2]nonene-2 (X, 17.0 g., 0.61 mole) in ether (20 ml.) was added dropwise to a suspension of lithium aluminum hydride (4.64 g., 0.12 mole) in ether (200 ml.). The mixture was stirred for 24 hr. and worked up in the usual way. The product, b.p. 102–103° at 12 mm., was purified by chromatography over alumina; 7.5 g. of a colorless oil was obtained, yield 61.5%.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>Br: C, 53.76; H, 6.46; Br, 39.80. Found: C, 54.26; H, 6.57; Br, 39.59.

*Bicyclo[3.2.2]nonane-3 (XIII).* 3-Bromobicyclo[3.2.2]nonene-2 (XII, 7.0 g., 0.035 mole) was dissolved in cold, concentrated sulfuric acid (20 ml.). The solution was stirred 48 hr., then poured into ice-water and extracted with ether. The ether extract, after drying, was evaporated. A crude oil was obtained, 5.1 g. The ketone was characterized by its 2,4-dinitrophenylhydrazone derivative, m.p. 153°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 56.63; H, 5.70; N, 17.60. Found: C, 56.87; H, 5.79; N, 17.42.

*Interaction of Dibromocarbene and 1-Methylnorbornene.* *exo-1-Methyl-3,4-dibromobicyclo[3.2.1]octene-2 (XIV) and exo-1-methyl-2,3-dibromobicyclo[3.2.1]octene-3 (XV).* A twofold excess of dibromocarbene was allowed to react with 1-methylnorbornene (30.0 g., 0.275 mole). Work-up gave an oil which was distilled (b.p. 106–108° at 2 mm.) to give 21.0 g. of product (25% yield). T.l.c. indicated that the product consisted of two components. The infrared absorption spectrum showed a maximum at 1640 cm.<sup>-1</sup>. The n.m.r. spectrum of the mixture showed that XV and XIV were the sole products of the reaction and were formed in a ratio of 1:4. The two broad areas centered at 170 and 105 c.p.s. are due to the bridgehead and methylene protons, respectively. The two sharp peaks at 82 and 74 c.p.s. are undoubtedly due to the different methyl groups of the two isomers. On the basis of peak intensities, the resonance at 82 c.p.s. can be assigned to the methyl group in XV and that at 74 c.p.s. to the methyl group of XIV. Integration of allylic and vinylic peak areas furnished the isomeric composition.

Several carbene additions to 1-methylnorbornene gave constant product composition as indicated by the n.m.r. spectra. XV (20.0%) and XIV (80%) were usually formed. Isomer XIV was obtained pure (as checked by the absence of XV through n.m.r. and by t.l.c.) by successive fractional distillation. The pure product (XIV) had b.p. 118° at 3.50 mm.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>Br<sub>2</sub>: C, 38.58; H, 4.32; Br, 57.10. Found: C, 38.37; H, 4.22; Br, 57.33.

Several samples of the XIV–XV mixture were passed through an Aerograph A 700 preparative chromatograph. Columns of Tide (detergent) and Carbowax (20 M) were used at temperatures of ca. 100°. Extensive decomposition occurred; the products were

collected and identified by their n.m.r. and mass spectra. Comparison with the behavior of authentic samples showed that the decomposition products were *m*-bromotoluene and ethylene.

*1-Methylbicyclo[3.2.1]octanone-3 (XVIII).* 1-Methyl-3,4-dibromobicyclo[3.2.1]octene-2 (XIV, 5.0 g., 0.018 mole) was added to a stirred solution of powdered lithium aluminum hydride in ether (18 ml.). The resultant mixture was refluxed for 12 hr. and worked up in the usual way. A colorless oil was obtained. It was dissolved in concentrated sulfuric acid (8 ml.) and was stirred at 0° for 2 days. The dark-colored solution was poured over crushed ice and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and then removed by evaporation; the resultant oil was distilled (1.7 g., 47.2% yield) b.p. 45–47° at 1.2 mm. T.l.c. indicated only one component. The infrared spectrum of the product showed a band at 1718 cm.<sup>-1</sup> (carbonyl).

The n.m.r. spectrum showed three kinds of protons: methyl (3H) at 68 c.p.s.; methylene (6H) centered at 99 and methylene (4H) centered at 131 c.p.s.; and bridgehead (1H) at 148 c.p.s. 1-Methylbicyclo[3.2.1]octanone-3 was characterized by its 2,4-dinitrophenylhydrazine derivative, m.p. 124°, and its dibenzylidene derivative, m.p. 189°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 56.60; H, 5.66; N, 17.61. Found: C, 56.38; H, 5.67; N, 17.30.

*Anal.* Calcd. for C<sub>23</sub>H<sub>22</sub>O: C, 87.90; H, 7.00. Found: C, 87.51; H, 6.70.

*Interaction of Dichlorocarbene and 1-Methylnorbornene.* *exo-1-Methyl-3,4-dichlorobicyclo[3.2.1]octene-2 (XVI) and 1-Methyl-2,3-dichlorobicyclo[3.2.1]octene-3 (XVII).* A typical reaction mixture consisted of 1-methylnorbornene (40.0 g., 0.37 mole), potassium *t*-butoxide (83.9 g., 0.74 mole), and chloroform (88.4 g., 0.74 mole). On work-up an oil was obtained, which was purified by fractional distillation (16.0 g., 23.0% yield), b.p. 50–55° at 0.1 mm. Infrared absorption spectrum of the neat liquid showed a maximum at 1625 cm.<sup>-1</sup>. T.l.c. showed the product to consist of two components. The n.m.r. spectrum indicated that XVI and XVII were the sole products of the reaction. There were two broad areas centered at 158 (bridgehead protons) and 101 c.p.s. (methylene protons). Two sharp peaks at 79 and 74 c.p.s. are due to the two non-equivalent methyl protons and correspond, respectively, to XVII and XVI. Table II records the details of the vinyl and allylic and methyl protons of the two isomers. Integration of the vinyl and allylic proton signal areas for the two isomers enabled their percentage composition to be determined. Several carbene additions were carried out and in each case the isomer composition of the products remained constant. XVII (57.0%) and XVI (43%) were usually formed. Attempted separation of the two isomers by vapor phase chromatography resulted in decomposition, even at low temperatures.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>Cl<sub>2</sub>: C, 56.50; H, 6.34; Cl, 37.20. Found: C, 56.50; H, 6.34; Cl, 36.87.

*Interaction of Dibromocarbene and 2-Methylnorbornene.* *3-Bromo-4-methylenebicyclo[3.2.1]octene-2 (XX).* A twofold excess of dibromocarbene generated by Doering's method was allowed to react with 2-methylnorbornene (32.4 g., 0.3 mole). Work-up gave an

oil which on distillation (b.p. 50–70° at 0.3 mm.) yielded 34.0 g. of crude product (46.8% yield). Redistillation gave 8.5 g. of product (b.p. 48° at 0.3 mm.) which v.p.c. showed to be a single component. However, t.l.c. indicated the presence of one other compound in a trace amount. The product (500 mg.) was purified by chromatography on silica (50.0 g.). Elution with ether–petroleum ether (3%) furnished 424 mg. of pure XX.

The infrared absorption spectrum of the neat oil showed maxima at 845, 890, 1450, 1625, 1780, 3038, and 3095 cm.<sup>-1</sup> which are completely concordant with the structure XX.

The ultraviolet absorption spectrum of XX in cyclohexane solution exhibited a single maximum at 242 mμ (ε 20,000).

The n.m.r. spectrum (in CDCl<sub>3</sub> solution) showed a broad multiplex signal at 104 c.p.s. due to methylene protons (6H); a broad signal at 157 c.p.s. due to a bridgehead proton (1H); a triplet centered at 185 c.p.s. (*J* = ~5 c.p.s.) due to another bridgehead proton (1H); and two vinyl singlets at 293 and 302 (2H) and another vinyl resonance at 391 (1H).

*Anal.* Calcd. for C<sub>9</sub>H<sub>11</sub>Br: C, 54.20; H, 5.52; Br, 40.20. Found: C, 53.47; H, 5.53; Br, 40.56.

It proved difficult to secure a better elemental analysis of XX, probably due to its remarkable facility to polymerize to a glassy solid even at 0°.

The carbene addition was repeated and the reaction mixture was worked up in the cold. T.l.c. showed that the product mixture consisted of two components (A, 40%, and B, 60%). One gram of the mixture of A and B was chromatographed on 40 g. of silica; rapid elution with ether–petroleum ether (2%) yielded pure B. The infrared absorption spectra of B showed no band in the 1625-cm.<sup>-1</sup> region. Gentle heating of B or standing at room temperature converted it to A which was shown by elemental analysis and its spectral properties to be XX. However, the ease of transformation of B to A and the subsequent facile polymerization of A made it difficult to characterize B further. On the basis of the above behavior it was reasonably assumed that B was the initial 1:1 adduct of dibromocarbene and 2-methylnorbornene (which is most likely formulated as XIX).

Hydrogenation of XX over Adams catalyst gave a colorless oil which was purified by microdistillation. Analysis indicated the uptake of three molecules of hydrogen per mole of XX with elimination of 1 mole of hydrogen bromide.

*Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>: C, 87.00; H, 13.00. Found: C, 86.87; H, 12.79.

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