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The Reaction of Bicyclo[2.2.2]octene with N-Bromosuccinimide

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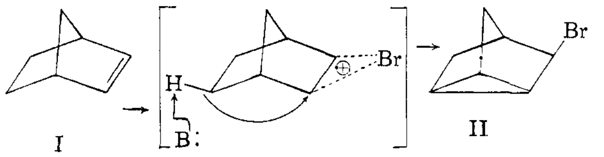
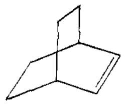
The reaction of bicyclo[2.2.2]octene (III) with N-bromosuccinimide produced a mixture of unsaturated monobromides and saturated dibromides. No bromohomonortricyclene was detected. The major component of the monobromide mixture was formulated as *endo*-8-bromobicyclo[3.2.1]oct-2-ene on the basis of degradative and solvolytic experiments and its structure is supported by n.m.r. and dipole moment data. The remaining monobromide component appears to be a mixture of *exo*- and *endo*-5-bromobicyclo[2.2.2]oct-2-ene. The isolation of tricyclo[2.2.2.0^{2,6}]octan-3-ol from the solvolysis is described. The predominant dibromide was found to be *trans*-2,3-dibromobicyclo[2.2.2]octane. The mode of formation of these products is discussed.

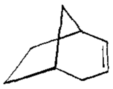
The Wagner–Meerwein relationship between the bicyclo[2.2.2]octan-2-yl and bicyclo[3.2.1]-octan-2-yl carbonium ions (as well as the corresponding unsaturated analogs) has been noted, but only recently have studies demonstrated that the interconversion involves a common bridged ("non-classical") carbonium ion.[2,3] The results suggested a close analogy with the corresponding norbornane (and norbornene) derivatives and the important differences have been attributed to the greater flexibility of the bicyclo[2.2.2]octane system relative to the bicyclo[2.2.1]heptane homolog.

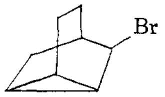
We have been interested in the comparative reactions of these two bicyclic systems, and this report describes one of our studies. The reaction of N-bromosuccinimide with norbornene (I) afforded major quantities of 3-bromonortricyclene (II).[4] The mechanism proposed for the formation of II was an ionic process as pictured below. Support for this mechanism came from the observation that the addition of hydrogen bromide markedly accelerated the reaction. The bromine thus formed from the reaction of NBS with hydrogen bromide would react with I to give II in much the same manner as did the direct addition of bromine to I. The objection to a free radical pathway is not as serious as first believed, since the findings of Dauben and McCoy have shown that bromine acts as an accelerator in allylic brominations.[5] The suggestion is that the homolysis of bromine (present in small concentrations), rather than a thermal or peroxide-catalyzed homolysis of NBS, initiates the substitution reactions.[6] These results prompted an investigation concerning the reaction of NBS with bicyclo[2.2.2]-octene (III). The bridgehead positions of III, as in I, preclude effective stabilization of the allylic radical intermediate. However, some differences in free radical reactions in the two systems are apparent in that chlorination of bicyclo[2.2.2]-octane, unlike the halogenation of norbornane, affords quantities of the bridgehead chloride.[7]



Bicyclo[2.2.2]octene (III) was prepared by the Diels–Alder addition of ethylene to 1,3-cyclohexadiene.[7,8,18] The diene was obtained from *trans*-1,2-dibromocyclohexane[3] and was carefully fractionated before use to avoid contamination by 3-bromocyclohexene. If these precautions were not taken the adduct formed was mainly bicyclo-[3.2.1]oct-2-ene (IV)[7] (15% III, 85% IV by gas chromatography), apparently produced by an acid-catalyzed isomerization of III.[7] Gas chromatographic analysis of III indicated little (<2%) contamination by the rearranged olefin IV; and hydrogenation of III gave bicyclo[2.2.2]octane.


III


IV



V

The reaction of bicyclo[2.2.2]octene (III) with an equimolar quantity of NBS was carried out in carbon tetrachloride employing benzoyl peroxide as a catalyst. During the four-hour reaction period, the mixture was irradiated with an ordinary light bulb. A mixture of monobromides was produced in yields of 24–31%. In addition, there was also obtained 8–9% of a mixture of dibromides.

SCHEME I

$$\begin{tikzcd}
\text{III} \arrow[r, "\text{NBS}"] & \text{monobromides (A)} + \text{dibromides} \arrow[dl, "\text{Na}/i\text{-PrOH}"'] \arrow[d, "H_2,\ \text{Pd}"] \arrow[dr, "Li_2CO_3/H_2O"] & \\
\text{IV} + \text{III} & \text{monobromides (B)} \arrow[d, "\text{KO}t\text{-Bu}"] & \text{VII} + \text{alcohols} \arrow[d, "H_2\text{Pd}"] \\
 & \text{VI} + \text{III} + \text{IV} & \text{VI}
\end{tikzcd}$$

Characterization of the monobromide mixture (A) was carried out as follows. Microanalysis supported an empirical formula $C_8H_{11}Br$. Sodium and alcohol reduction produced a hydrocarbon mixture consisting of 74% IV and 26% III. The infrared spectrum of A did not show bands "characteristic"

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[1] Department of Chemistry, Oklahoma State University, Stillwater, Okla.

[2] H. M. Walborsky, M. E. Baum and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).

[3] (a) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961); (b) **83**, 1992 (1961); (c) H. L. Goering, R. W. Greiner and M. F. Sloan, *ibid.*, **83**, 1391 (1961).

[4] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[5] H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, **81**, 4863 (1959).

[6] For an alternative mechanism for allylic NBS brominations see B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

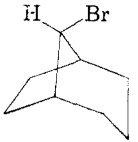
[7] A. F. Bickel, J. Knotnerus, E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960); *cf.* also E. C. Kooyman and G. C. Vegter, *ibid.*, **4**, 382 (1958).

[8] J. Hine, *et al.*, *J. Am. Chem. Soc.*, **77**, 594 (1955).

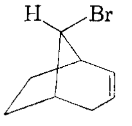
of a 3-bromohomonortricyclene (V).[9] Analysis by gas chromatography indicated that A was composed of at least two components as indicated by the appearance of two peaks in the ratio 78:22. After catalytic reduction of A, a new mixture (B) of saturated monobromides was obtained. Once again, gas chromatography showed two components (74:26). Apparently the major constituent of mixture A was a bromobicyclo[3.2.1]octene. Consequently, B was subjected to vigorous dehydrobromination conditions. There was formed olefin III containing *ca.* 15% of the isomer IV. In addition, a pure, unreactive, saturated monobromide (VI) was obtained. Gas chromatography showed that this product corresponded to the major component of B; and debromination of VI gave bicyclo[3.2.1]octane.

Solvolysis of mixture A with aqueous lithium carbonate produced a mixture of alcohols in 22–32% yield and an unreactive monobromide (VII). These products were separated by chromatography on alumina. Debromination of VII gave exclusively bicyclo[3.2.1]oct-2-ene (IV). Catalytic hydrogenation of VII gave a crystalline compound that was identical with VI as evidenced by melting point behavior, infrared spectra and gas chromatography. Compound VI was recovered in high yield from attempted dehydrobromination with potassium *t*-butoxide.

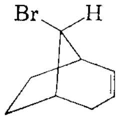
On the basis of these results, monobromide VI must contain the bicyclo[3.2.1]octane skeleton and the component of mixture A from which it was derived must be a bromobicyclo[3.2.1]oct-2-ene. Only structures VII–X, having the bromine attached at the bridgehead or the one-carbon bridge, can satisfy these data. The bridgehead compounds, 1-bromobicyclo[3.2.1]oct-2-ene (IX) and 5-bromobicyclo[3.2.1]oct-2-ene (X), were eliminated on the basis of the n.m.r. spectrum of VI. The spectrum shows a symmetrical triplet at τ = 5.87 corresponding to a secondary bromide with two equivalent hydrogen atoms in the α-position. A determination of the dipole moment of VI and the unsaturated monobromide (VII or VIII) served to eliminate VIII as a possibility. A value of μ = 2.09 D. was obtained for VI and this value was used for the carbon–bromine bond moment in calculations of the dipole moments of structures VII and VIII. A value of 0.40 D. was used as the contribution due to the double bond.[10] The calculations were made with the aid of the diagram of Fig. 1. Using values (estimated from Dreiding stereomodels) of 30, 60, and 170° for the angles θ, ϕ and β, respectively, the calculated moment of VII is 2.28 D. and that of VIII is 1.75 D. The observed value of 2.13 D. is consistent only with structure VII. Hydrogenation would be expected to decrease the moment of VII, and a very small lowering was noted. The proton magnetic resonance spectrum is consistent with structure VII with bands appearing at 4.47 τ (vinyl protons) and 6.00 τ (triplet, *H*–C–Br).



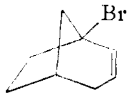
VI



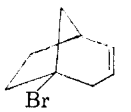
VII



VIII



IX



X

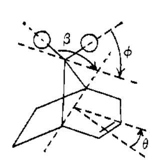
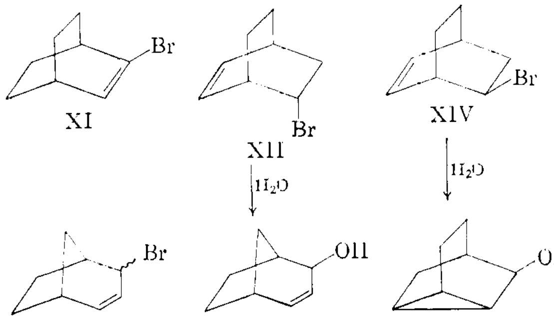


Fig. 1.

Additional chemical evidence in support of structure VII and of VI is the resistance of these bromides toward solvolysis. When VI was heated with aqueous silver nitrate solution an alcohol was isolated which was shown to be identical with *exo*-bicyclo[3.2.1]octan-8-ol.[11]

The observation that the dehydrobromination of mixture B produced III as the major olefin component suggested that mixture A contained at least one other monobromide having a bicyclo-[2.2.2]octene carbon skeleton Possibilities are 2-bromo- (XI) and *endo*- and *exo*-5-bromobicyclo-[2.2.2]oct-2-ene (XII and XIV, respectively). Compound XI was prepared as described below and could be rejected by gas chromatographic analysis. The alcohol fraction, formed from the solvolysis of mixture A, consisted of a mixture of *exo*-(axial)-bicyclo[3.2.1]oct-3-en-2-ol (XIII) and a higher melting isomer (XV). From the results of the solvolytic studies of the corresponding tosylate,[3c] we presume that the allylic alcohol XIII most probably arises from solvolysis of the *endo*-unsaturated bromide XII. The isomeric alcohol XV was unique in that it failed to give qualitative tests for unsaturation and did not absorb hydrogen on attempted catalytic reduction. Microanalysis indicated the empirical formula $C_8H_{12}O$, and the infrared spectrum showed bands at 3390, 1005, 990, 812 and 798 cm.$^{-1}$. Oxidation with chromium trioxide afforded a ketone which was isolated as the semicarbazone. Formulation of this product tricyclo[2.2.2.0^{2,6}]octan-3-ol (XV, "homonor-



XI XII XIV XVI XIII XV

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[9] A. Gagneux and C. A. Grob, *Helv. Chim. Acta*, **42**, 1753 (1959).

[10] N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

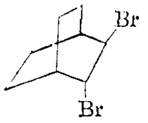
[11] A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 4299 (1960).

tricyclanol") is also supported by the n.m.r., spectrum in that a complex multiplet shows at 9.07 τ which we assign to the cyclopropane hydrogen atoms. Alcohol XV could have conceivably arisen from solvolysis of bromide V if the latter were present as a minor component of mixture A. However, we tentatively conclude, based on the product balances obtained from the reactions outlined in Scheme I and after careful examination of the infrared spectra and gas chromatograms of this mixture, that XV results from solvolysis of *exo*-5-bromobicyclo[2.2.2]oct-2-ene (XIV).

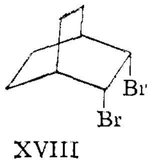
It becomes necessary to account for the production of amounts of bicyclo[3.2.1]oct-2-ene (IV) in the dehydrobromination of mixture B. An obvious conclusion is that mixture A contains small amounts of an additional bicyclo[3.2.1]octene monobromide. This product is assigned the structure 2-bromobicyclo[3.2.1]-oct-3-ene (XVI) and an authentic sample was obtained from the reaction of IV with NBS. We attribute the formation of XVI to a direct bromination of olefin IV present as a contaminant in III; further support is given by the fact that upon reacting less pure samples of III with NBS, larger amounts of bicyclo[3.2.1]oct-2-ene (IV) are observed in the products of dehydrobromination of the corresponding fraction B.

The crude distilled mixture of dibromides from the *N*-bromosuccinimide reaction was found to contain approximately 26% (by weight) of an adduct which decomposed when the mixture was allowed to stand for several days. The presence of this adduct was inferred by infrared examination which showed N-alkylsuccinimide absorption. On decomposition, bromide VII and succinimide were produced. This result suggests that at least a part of the rearranged "free radicals" are trapped by succinimide radicals before hydrogen abstraction can take place.[12]

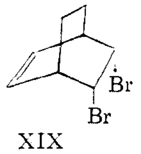
The major dibromide (82%) produced in the reaction of III with NBS has been shown to be *trans*-2,3-dibromobicyclo[2.2.2]octane (XVII). This assignment is based on the following evidence. Treatment of XVII with sodium and alcohol or with zinc gave III as the only product. Dehydrobromination produced XI. This vinyl bromide was characterized by conversion to the known bicyclo[2.2.2]-octan-2-one on hydrolysis. A dipole moment determination for the solid dibromide XVII gave a value of 2.77 D. which suggests a *trans* arrangement of the bromine atoms. The measured moment for *trans*-2,3-dibromonorborane is 2.50 D.[13] and the difference is attributed to the greater flexibility of the bicyclo[2.2.2]octane homolog which allows a decrease in the dihedral angle of XVII.



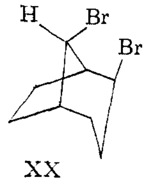
XVII



XVIII



XIX



XX

The presence of the *cis*-dibromide XVIII could be excluded by gas chromatographic studies with a known sample. A Diels–Alder addition of 1,2-dibromoethylene to 1,3-cyclohexadiene produced a mixture of adducts from which *endo-cis*-5,6-dibromobicyclo[2.2.2]oct-2-one (XIX) was isolated, μ = 3.31 D. Catalytic hydrogenation of XIX afforded the crystalline saturated dibromide XVIII. The remainder of the adduct from which XIX was isolated was a liquid which was also hydrogenated. The mixture obtained was analyzed by gas chromatography and was found to consist of at least four components. The major dibromide components could be identified as XVII and an isomer which was identical with a second dibromide obtained from the NBS reaction. The nature of this presumed "rearranged" dibromide, present in the NBS dibromide fraction in amounts of about 10%, was deduced from the following evidence. The addition of bromine in carbon tetrachloride to III at −4° produced a mixture of dibromides of which XVII was the major component (86%). In addition, small amounts of 2-bromobicyclo[2.2.2]octane (XXII) and 2-bromobicyclo[3.2.1]octane (XXIII) were isolated. There latter monobromides are presumed to arise *via* the generation of hydrogen bromide and addition to III. Much of the *trans*-dibromide XVII was removed from the mixture by crystallization. Dehydrobromination of the mother liquors gave a mixture of XI (51%) and VII (20%). On this basis, we formulate the contaminating dibromide as the rearranged *exo-syn*-2,8-dibromobicyclo[3.2.1]octane (XX). It should be noted that XX was a minor component of the dibromide mixtures from the NBS reaction, the bromination and the hydrogenated Diels–Alder reaction mixture. When the bromination of III was carried out in the presence of one-half molar equivalent of pyridine. XVII was the *only* dibromide detected. However, a single monobromide, identical with *endo*-8-bromobicyclo[3.2.1]oct-2-ene (VII), was formed in 12% yield.

It is interesting to speculate on the mechanism of formation of VII, particularly in view of the possibility that if a free radical path were involved it would constitute a free radical rearrangement as the major course of the reaction. Recently, studies of the decomposition of 2,2′-bis-azocamphane have demonstrated a formal free radical analog of the Wagner–Meerwein carbonium ion rearrangement.[14] Quite obviously, the unrearranged monobromides XII and XIV must arise from the radical XXI. The observation that XXI is not brominated to any appreciable extent in the "homoconjugative" manner to give V is a re-

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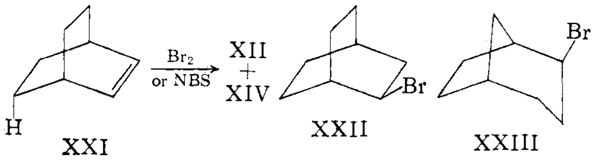
[12] Evidence for the production of an adduct as the major course of the reaction of *endo*-3,6-methanotetrahydrophthalic anhydride with NBS has been obtained; L. H. Zalkow, unpublished results. It is conceivable, however, that such adducts may result from an ionic addition of NBS to the olefin.

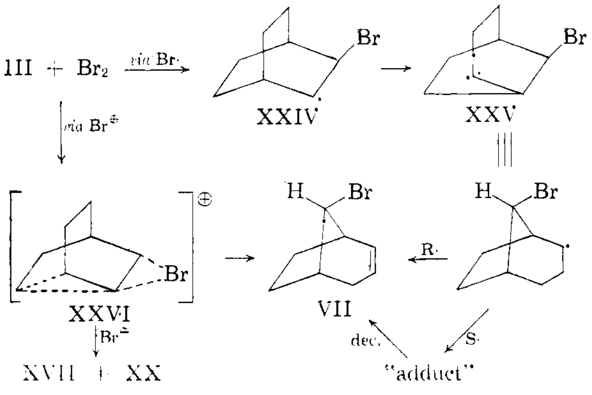
[13] N. A. LeBel and E. Karger, unpublished results.

[14] J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).



flection of the fact that little relief of strain would be gained as compared with the norbornyl–nortricyclyl interconversion. In addition, our failure to detect bridgehead substitution products of III suggests that the olefin is a more rigid species than its saturated analog. Scheme 2 presents several mechanistic possibilities leading toward the remaining products. Both processes have been represented as involving molecular bromine. The homolytic sequence would require the addition of a bromine radical to the olefin to give the intermediate XXIV. Rearrangement followed by hydrogen abstraction would afford the rearranged monobromide VII. The dibromides may arise from either of these intermediates. Reaction of succinimidyl radical with XXV would afford an adduct which could be visualized as decomposing to yield VII and succinimide. These steps are consistent with the Goldfinger mechanism as recently put forth by McGrath and Tedder,[6] except that we visualize succinimidyl radicals as discrete intermediates.

SCHEME 2



In an attempt to generate the intermediate radicals in Scheme 2 in another fashion, we have re-examined the free radical addition of hydrogen bromide to bicyclo[2.2.2]octene (III).[15] The reaction of III with hydrogen bromide in pentane and benzoyl peroxide as the catalyst afforded a mixture of 2-bromobicyclo[2.2.2]octane (XXII) and 2-bromobicyclo[3.2.1]octane (XXIII). The ratio of these two products, 79:21, respectively, was determined by dehydrobromination and gas chromatographic analysis of the hydrocarbons III and IV which were produced. No VI was detected. The rearranged bromide must result from an ionic addition and we have no way of discerning the relative amounts of competing ionic and free radical addition processes. Nevertheless, our failure to detect products from the rearranged free radical XXV cannot be taken as evidence against its occurrence in the NBS reaction. It is very reasonable to assume that XXIV reacts with hydrogen bromide in the chain transfer step at a rate much faster than it can rearrange to XXV. The thiophenol addition to III afforded a non-rearranged phenyl thioether.

An ionic process is equally, if not more, attractive. Formation of the bridged ion XXVI (one of several possible structures) is followed by loss of a proton to give VII or by reaction with bromide to give the *trans* and rearranged dibromides XVII and XX, respectively. The stereochemistry of these products is conveniently accounted for. The production of VII is quite analogous to the formation of 3-bromonortricyclene (II).[4]

The ultimate solution to the question of an ionic or free radical pathway for this unique bromination must rest in further investigation. It can be convincingly stated, however, that the NBS bromination of olefins having bridgehead allylic hydrogen atoms results in the generation of appreciable amounts of bromine in the reaction mixture.

Acknowledgment.—This study was supported by a generous grant from the Research Corporation.

Experimental[16]

Gas Chromatographic Analysis.—Three standard columns of 6′ × 8 mm. Pyrex were employed: column A was packed with 25% by weight of γ-nitro-γ-methylpimelonitrile suspended on 30–80 mesh base-washed firebrick; column B, 25% Silicone 550 fluid on firebrick; column C, 25% of triethylene glycol saturated with silver nitrate on 42–60 mesh base-washed firebrick. Column B was pre-conditioned by the injection of several samples of bicyclic dibromides followed by a large sample of di-*n*-butylamine. The carrier gas was helium.

Bicyclo[2.2.2]oct-2-ene (III).—1,3-Cyclohexadiene (80% pure as shown by gas chromatography) was prepared from 1,2-dibromocyclohexane.[8] The diene (containing 1 mole % of pyridine[7]) was treated with ethylene in a steel autoclave at 240–250° and bicyclo[2.2.2]oct-2-ene (III) was isolated by fractional distillation through a 2.5 × 30 cm. Vigreux column (121 g., 38%); b.p. 133–135° (lit. b.p. 130–135°,[8] 133–135°[7]). A sample was sublimed from anhydrous sodium sulfate: m.p. 113–114.5° (lit. m.p. 116.4–117.5°,[8a] 112–113°[7]). Gas chromatography on column C at 51° indicated >98% III and <2% IV. At a flow rate of 120 cc./min., the retention times of III and IV are 15.3 and 11.6 min., respectively.

Bicyclo[2.2.2]octane.—A 4.0-g. (0.037 mole) sample of III was hydrogenated at atmospheric pressure in 50 ml. of absolute ethanol employing 470 mg. of pre-reduced platinum oxide as a catalyst. A quantitative amount of hydrogen was absorbed in 30 minutes. The catalyst was removed by filtration, and water was added to the filtrate to precipitate the hydrocarbon. The product was collected by filtration (2.94 g., 73%). In order to obtain a pure sample of the octane, a portion of the product was pressed between two sheets of filter paper and was then sublimed from phosphorus pentoxide to give pure bicyclo[2.2.2]octane, m.p. 169–171.5° (lit. 169–170°[17] and 168–171°[18]).

The Reaction of Bicyclo[2.2.2]oct-2-ene (III) **with N-Bromosuccinimide.**—A typical reaction was carried out as follows. A mixture of 40.0 g. (0.370 mole) of III, 65.8 g. (0.370 mole) of N-bromosuccinimide, 1 g. of benzoyl peroxide and 200 ml. of dry carbon tetrachloride was heated to reflux temperature for 4 hours with stirring. During this period the mixture was irradiated with a 100-

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[15] H. M. Walborsky, *Experientia*, **9**, 209 (1953).

[16] All melting points are corrected and boiling points are uncorrected. Sealed capillaries were used in the melting point determinations of the bicyclic hydrocarbons, olefins, bromides and alcohols. The infrared spectra were obtained on a Beckman model IR 4 recording spectrophotometer with sodium chloride optics. The dipole moment determinations were made by Miss M. A. DaRooge. Analyses are by Midwest Microlabs, Inc., Indianapolis, Ind.

[17] K. Alder and G. Stein, *Ann.*, **514**, 1 (1934).

[18] H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76** 5396 (1954).

watt G.E. spotlamp. The reaction mixture was filtered and the solids were washed thoroughly with carbon tetrachloride. The combined filtrate and washings were washed with three 50-ml. portions of water to remove all traces of succinimide. The organic layer was dried and concentrated by distillation through a 2.5 × 30 cm. Vigreux column. The last traces of solvent along with unreacted, unrearranged III (5.5 g.) were removed *in vacuo*. Fractionation of the residue, employing a 0.8 × 60 cm. tantalum spiral column, gave 15.32 g. of monobromide fractions, b.p. 65–70.5° (6 mm.); 1.97 g. of an intermediate fraction, b.p. 70.5° (6 mm.) –87° (1.1 mm.); and 14.47 g. of dibromide fractions, b.p. 87–96° (1.1–1.3 mm.). A trace of white solid (31 mg.) was observed in the monobromide fractions which was removed by filtration and purified by recrystallization from chloroform. Its melting point of 124–126° showed no depression upon admixture with succinimide. The monobromide fractions were dissolved in 50 ml. of pentane and the solution was washed with three 20-ml. portions of water, dried over anhydrous magnesium sulfate and concentrated. Refractionation of the monobromide material gave the fractions

Fraction	Wt., g.	*t*, °C. (6 mm.)	n^{25}D
1	0.55	67.0–67.5	1.5349
2	2.86	67.5	1.5361
3	2.39	67.5–69	1.5367
4	6.11	69.0–70	1.5378
5	2.19	70.0–70.5	1.5389

Each of these fractions formed an immediate precipitate on treatment with alcoholic silver nitrate solution and rapidly decolorized a solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93; Br, 42.72. Found: C, 51.67; H, 6.08; Br, 43.03.

Gas chromatography on column B at 148.5°, flow rate 76 cc./min., indicated two peaks in the ratio 78:22 with retention times of 13.8 and 12.5 minutes, respectively.

The infrared spectrum of the dibromide fractions showed a strong band at 1715 cm.$^{-1}$, but no band in the N-H stretching region. A similar spectrum was obtained on the reaction mixture before distillation. When the dibromides were allowed to stand for several days, a white solid formed which was shown by melting point and mixed melting point to be succinimide. Employing the same separation and purification technique as described for the monobromide fractions, a total of 0.2 g. of succinimide was obtained. The dibromides were refractionated and the following fractions were collected

Fraction	Wt., g.	*t*, °C. (3.25 mm.)	n^{23}D
6	2.58	55–58	1.5385
7	3.12	100–102	....
8	6.08	102–105	....

Fractions 7 and 8 were combined and taken as the dibromide mixture (9.2 g., 9.3%). Gas chromatographic analysis of fraction 6 was identical with that of fractions 1–5, except that the ratio of components was found to be 91:9.

A crystalline dibromide, *trans*-2,3-dibromobicyclo[2.2.2]-octane (XVII) (2.2 g.), was separated from the dibromide mixture by trituration with pentane; m.p. 55.0–55.5°. An additional 0.3 g. of XVII was obtained by concentration and distillation of the mother liquors.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64. Found: C, 36.12; H, 4.56; Br, 59.75.

A second distillation furnished 3.0 g. of liquid dibromide mixture. b.p. 103–108° (3.7 mm.), n^{21}D 1.5657.

The infrared spectrum (carbon disulfide solution) of the liquid dibromide mixture has all of the bands characteristic of the spectrum of XVII. Gas chromatography on column B at 180°, flow rate 60 cc./min., indicated the presence of XVII (56%), 2,8-dibromobicyclo[3.2.1]octane (XX) (25%) and unknown components (19%).

Several other runs were made and the results were analogous. In one case, careful fractionation of the reaction mixture gave a complete separation of the monobromides (31% yield). Removal of succinimide from the dibromide mixture and careful redistillation led to VII as the only monobromide present.

No significant differences were noted when the reagents were carefully purified just prior to use in the reaction of II with N-bromosuccinimide.

Hydrogenation of Mixture A.[19]—Employing 60 mg. of prereduced platinum oxide as a catalyst, 0.50 g. (2.7 mmoles) of the monobromide mixture in 15 ml. of absolute ethanol was allowed to take up exactly one equivalent of hydrogen. The hydrogenation was stopped after 15 minutes and the catalyst was removed by filtration. The ethanolic filtrate was diluted with 150 ml. of water and the product was extracted with 30 ml. of pentane. The pentane layer was washed twice with water, dried and concentrated by distillation through a 1.2 × 10 cm. Vigreux column.

Gas chromatography of the residue (column A at 134°, flowrate of 77 cc./min.) indicated two peaks in the ratio 74:26 with retention times of 25.5 and 27.5 minutes, respectively.

After removal of the last traces of pentane from the residue *in vacuo*, 355 mg. (70%) of white solid remained, m.p. 65.5–68.5°. Sublimation of a sample did not change the melting point. The product showed no unsaturation but did give a precipitate with alcoholic silver nitrate solution.

A second hydrogenation was allowed to proceed until the uptake of hydrogen had ceased. Under these conditions, 1.11 equivalents of hydrogen was absorbed and the solid obtained after work-up melted at 79–80°. Gas chromatography (as described above) showed two peaks in the ratio 83:17.

Sodium and Alcohol Reduction of Mixture A.—Sodium metal (1.36 g.) was added to a solution of mixture A (0.50 g., 2.7 mmoles) in 15 ml. of dry isopropyl alcohol and the mixture was refluxed for 4 hours. The reaction mixture was allowed to cool to room temperature and was carefully diluted with water. The aqueous solution was extracted with three 30-ml. portions of pentane. The combined pentane solutions were washed with water and dried. Removal of the pentane by distillation afforded *ca.* 0.5 g. of residue. The residue readily decolorized a solution of bromine in carbon tetrachloride. Gas chromatographic analysis on column A at 64° indicated the presence of 74% of IV and 26% of III.

Dehydrobromination of Mixture B.[20]—A 436-mg. (2.3 mmoles) sample of mixture B was treated with an equimolar amount of potassium *t*-butoxide (from 90 mg. of potassium metal dissolved in 6 ml. of boiling dry *t*-butyl alcohol). The solution was heated at reflux for 20 hours, and was worked up in the usual manner. Gas chromatography of the residue (0.3 g.) on column A at 134° indicated only one peak which was identical with the larger of the two peaks from the chromatogram of mixture B, described above. Chromatography of the residue on the column at 64° indicated the presence of both olefins III and IV, in the ratio of 83% to 17%, respectively. At this low temperature the bromide could not be detected.

Employing a low temperature recrystallization apparatus, the bromide was precipitated from a solution of the residue in pentane. An additional recrystallization from pentane afforded 53 mg. of crystalline *endo*-8-bromobicyclo[3.2.1]-octane (VI), m.p. 89.5–90.0°, m.m.p. 89–90°.

Solvolysis of Mixture A.—A mixture of 5.00 g. (26.7 mmoles) of mixture A, 4.6 g. of lithium carbonate and 45 ml. of water was heated at reflux for 3 days with stirring by means of a magnetic stirrer. About 5 ml. of dioxane was added to the refluxing mixture in order to prevent accumulation of bicyclic material in the condenser. After filtering, the solids were washed with ether. The filtrate and washings were diluted with 200 ml. of water and extracted with three 50-ml. portions of ether and one 50-ml. portion of pentane. The combined extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated by distillation. The residue (about 5 g.) was dissolved in pure pentane and the solution was placed on a column containing 200 g. of Merck acid-washed alumina. Elution with 1400 ml. of pure pentane afforded, after evaporation of the solvent followed by distillation of the residue, 3.14 g. (63%) of *endo*-8-bromobicyclo[3.2.1]oct-2-ene (VII), b.p. 70–71.5° (6.2 mm.), n^{24}D 1.5378.

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(19) The monobromide fractions from the N-bromosuccinimide reaction are referred to as mixture A.

(20) The saturated monobromides from the hydrogenation (one equivalent of hydrogen) of mixture A are referred to as mixture B.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93; Br, 42.72. Found: C, 51.59; H, 5.87; Br, 42.38.[21]

No precipitate formed on treatment of VII with alcoholic silver nitrate solution. The infrared spectrum (CS_2) of VII shows all of the strong bands formed in the spectrum of mixture A and many of the weak bands present in the spectrum of mixture A are absent entirely from the spectrum of VII. Those bands characteristic of VII appear at 1305(m), 1250(m), 1220(s), 1180(m), 1010(w), 905(m), 845(m), 810(m), 720(s) and 675(s) cm.$^{-1}$.

Further elution of the column with 7000 ml. of 10% anhydrous ether in pentane yielded only traces of material (*ca.* 80 mg.). An additional 1800 ml. of 10% ether–pentane, followed by 800 ml. of 25% ether–pentane, afforded 210 mg. of *exo*-(*axial*)-bicyclo[3.2.1]oct-3-en-2-ol (XIII), m.p. 78.5–92.5°. Three recrystallizations from pentane at low temperature afforded crystalline alcohol, m.p. 86.5–89.1° (lit.[3c] m.p. 85.5–87.0°). The *p*-nitrobenzoate melted at 81.5–82.7° (lit.[3] m.p. 86.2–86.6°) after one recrystallization from aqueous ethanol (78% yield). The infrared spectrum of XIII was consistent with that reported.[3c]

Continued elution with 1200 ml. of 25% ether–pentane furnished 320 mg. of a mixture of alcohols. Analysis by gas chromatography on a Tide column[3] indicated two components: 33% of XIII and 67% of an isomer (XV). Pure tricyclo[2.2.2.$0^{2,6}$]octan-3-ol (XV) (200 mg.) was isolated from the next seven fractions (1400 ml. of 25% ether–pentane), m.p. 125–127.1° after sublimation. The retention times for XIII and XV at 142° are 12.6 and 18.3 minutes, respectively.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.26; H, 9.73.

The *p*-nitrobenzoate was prepared and was recrystallized three times from ethanol; m.p. 84.1–84.9°.

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.66; H, 5.36; N, 5.17.

The column was washed with ether and an additional 100 mg. of oil was obtained, which by gas chromatography was found to consist chiefly of alcohol XV.

Tricyclo[2.2.2.$0^{2,6}$]octan-3-one from Tricyclo[2.2.2.$0^{2,6}$]-octan-3-ol (XV).—One hundred and fifty milligrams of XV was oxidized with chromium trioxide in acetic acid according to the procedure of Roberts, *et al.*[4] The steam distillate was extracted with two 25-ml. portions of pentane and the combined extracts were dried over anhydrous magnesium sulfate and concentrated by distillation. The residue (113 mg.) contained 79% of tricyclo[2.2.2.$0^{2,6}$]octan-3-one and 21% XV as shown by gas chromatography on the Tide column. The impure ketone was treated with semicarbazide hydrochloride by the usual procedure and, after two recrystallization from aqueous ethanol, 25 mg. of the semicarbazone was obtained, m.p. 187.5–188.1°.

Anal. Calcd. for $C_9H_{13}ON_3$: C, 60.32; H, 7.31; N, 23.45. Found: C, 60.36; H, 7.36; N, 23.65.

The semicarbazone was also obtained when XV was oxidized with chromium trioxide in pyridine.

endo-8-Bromobicyclo[3.2.1]octane (VI).—A solution of 1.00 g. (5.4 mmoles) of VII in 20 ml. of absolute ethanol was hydrogenated (quantitative uptake of hydrogen) in the presence of 100 mg. of prereduced platinum oxide. Isolation of the product was carried out as described above. After several recrystallizations from methanol, 606 mg. (60%) of *endo*-8-bromobicyclo[3.2.1]octane (VI) was obtained, m.p. 90–90.5°. The infrared spectrum (CS_2) shows major bands at 1320(m), 1220(s), 985(m), 885(m), 825(m), 765(w), 750(s) and 680(w) cm.$^{-1}$. Gas chromatography indicated one peak with a retention time identical with the larger of the two peaks in the chromatogram of mixture B.

Anal. Calcd. for $C_8H_{13}Br$: C, 50.81; H, 6.93; Br, 42.26. Found: C, 51.06; H, 7.08; Br, 41.86.

Sodium and Alcohol Reduction of *endo*-8-Bromobicyclo-[3.2.1]oct-2-ene (VII).—Employing a procedure similar to that described above, 1.0 g. (5.4 mmoles) of VII was debrominated. After the work-up, the residue was chromatographed directly on column A at 64°. The only hydrocarbon detected was IV. A sodium fusion determination on the residue showed the absence of any unreacted bromide.

Sodium and Alcohol Reduction of *trans*-2,3-Dibromobicyclo[2.2.2]octane (XVII).—The method employed for the debromination of 700 mg. (2.6 mmoles) of XVII was the same as that described for the reduction of mixture A. Gas chromatography of the residue on column A at 68° indicated only the presence of III. Removal of the last traces of pentane *in vacuo* and sublimation of the residue gave III, m.p. 109–111°.

2-Bromobicyclo[2.2.2]oct-2-ene (XI).—Two grams (7.5 mmoles) of XVII was heated under reflux with potassium *t*-butoxide (from 292 mg. of potassium and 15 ml. dry *t*-butyl alcohol) for 16 hr. The work-up of the reaction was carried out in the manner described above for the dehydrobromination of mixture B. Distillation of the residue produced 900 mg. (64%) of 2-bromobicyclo[2.2.2]oct-2-ene (IX), b.p. 64–65° (6 mm.), $n^{21}\text{D}$ 1.5318.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93; Br, 42.72. Found: C, 51.13; H, 6.03; Br, 42.63.

Gas chromatography of XI through column B at the same conditions as that used for mixture A showed one peak with a retention time of 10.9 minutes.

Solvolysis of XI.—A sample (400 mg., 2.14 mmoles) of XI was refluxed with 282 mg. of lithium carbonate in 12 ml. of water for a period of 7 days. The product was steam distilled from the reaction mixture and the distillate was extracted with two 15-ml. portions of ether. The ether solutions were combined and dried. The solvent was removed and the residue was added to sufficient 2,4-dinitrophenylhydrazine reagent to convert all of the product to the hydrazone. The crude derivative (m.p. 144–146°) was dissolved in a small amount of pure benzene and placed on a column of Merck acid-washed alumina (4.0 g.). Elution with 100 ml. of benzene followed by evaporation of the solvent gave a crystalline derivative. Three recrystallizations from 95% ethanol afforded the orange 2,4-dinitrophenylhydrazone of bicyclo[2.2.2]octane-2-one, m.p. 163–164° (lit.[18] m.p. 166–167°).

The Radical Addition of Hydrogen Bromide to Bicyclo-[2.2.2]octene.—A solution of 3.00 g. (0.0277 mole) of III and 67 mg. (1 mole %) of benzoyl peroxide in 100 ml. of purified pentane was cooled to 0° and gaseous hydrogen bromide (dry) was bubbled through at a slow rate for 1 hr. The reaction mixture was allowed to warm to room temperature and was stirred for 6 hr. The mixture was washed with two 50-ml. portions of 5% sodium bicarbonate solution followed by two 50-ml. portions of water, dried over anhydrous magnesium sulfate and concentrated. Distillation of the residue produced 4.33 g. (83%) of product, b.p. 88.5–91° (10 mm.), m.p. 61–62°. Recrystallization from methanol gave a gummy solid melting at 64.0–64.5°.[22]

Gas chromatography of this monobromide mixture (C)[23] on column A at 134° indicated one peak which has a retention time identical with the smaller of the two peaks in the chromatogram of mixture B.

Dehydrobromination of Mixture C.—One hundred milligrams (0.53 mmole) of mixture C was treated with an equimolar quantity of potassium *t*-butoxide in the manner described for the dehydrobromination of mixture B.

The presence of both olefins III and IV in the ratio of 79:21, respectively, was indicated by gas chromatography of the residue.

The Addition of Bromine to Bicyclo[2.2.2]oct-2-ene (III).—A solution of 10 g. (92.5 mmoles) of III in 20 ml. of dry carbon tetrachloride was placed in a three-necked flask fitted with a stirrer, a thermometer and a dropping funnel. To this was added dropwise 14.77 g. (92.5 mmoles) of bromine in 15 ml. of dry carbon tetrachloride. The addition required 2 hours during which time the temperature was maintained at −4° by means of an ice–salt-bath. The reaction mixture was allowed to stand overnight and a slight trace of hydrogen bromide was detected. The carbon tetrachloride solution was washed with 20 ml. of a saturated sodium bicarbonate solution followed by two 20-ml. portions of water and was dried over anhydrous sodium sulfate. The solvent was removed by distillation. Fractionation of the residue produced 2.25 g. (13%) of saturated monobromides, b.p. 72–76° (6 mm.), and 15.70

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(21) Bromine was determined by these authors.

(22) W. von E. Doering and M. Farber, *J. Am. Chem. Soc.*, **71**, 1514 (1949). These authors report the melting point of XXII as 64–65.5° and that of XXIII as 39–41°.

(23) The product from the hydrogen bromide addition to III is referred to as mixture C.

g. (63%) of dibromide fractions, b.p. 77° (1.2 mm.) –78° (0.3 mm.). The monobromide fraction (mixture D) solidified and after two recrystallizations from methanol, and sublimation from phosphorus pentoxide gave a product melting at 61–64°.

Only one peak was obtained upon gas chromatography of mixture D on column A at 134°, and its retention time was identical with that of mixture C. The infrared spectrum of mixture D was identical with the spectrum of mixture C and a mixed melting point determination showed no depression. Dehydrobromination with potassium *t*-butoxide produced olefins III and IV in the ratio 67:33.

The dibromide fractions contained solid material and they were treated in the same manner as the dibromide fractions from the reaction of III with N-bromosuccinimide. After the procedure had been carried out twice, a total of 3.48 g. of XVII was isolated, m.p. 55.0–55.5°, m.m.p. 54.5–55.5°. The infrared spectrum of XVII (CS_2) shows major bands at 1280(s), 1235(w), 1205(w), 1160(s), 952(s), 824(m) and 762(s) cm.$^{-1}$.

Redistillation of the mother liquors afforded 5.70 g. of liquid dibromide(s), b.p. 88–103° (3 mm.), n^{25}D 1.5561. The infrared spectrum was similar to the spectrum of XVII. Gas chromatography of this mixture on column B at 180° indicated three components, XVII, XX and an unknown product in the ratio 68:19:13, respectively.

When the addition of bromine to III (2.5 g., 23.1 mmoles) was carried out in the presence of pyridine (0.91 g., 11.5 mmoles), no saturated monobromide products were formed, as expected. Gas chromatography of the residue after the work-up on column B indicated 12% of VII and 88% of XVII.

The Diels–Alder Addition of Dibromoethylene to Cyclohexadiene.—Two-thirds of a mixture of 95 g. (1 mole, material of 85% purity) of 1,3-cyclohexadiene and 185.9 g. (1 mole) of 1,2-dibromoethylene were placed in the glass liner (120-ml. capacity) of a stainless steel reaction vessel under 500 p.s.i.g. nitrogen pressure. The charge was heated to 200° for 8.5 hours. The remainder of the reaction mixture was similarly treated, but this time the charge was heated to 220° for 8 hours. The reaction products were combined and the bulk of the low boiling material was removed by distillation at atmospheric pressure. Fractionation of the high boiling material gave 16.42 g. (6.2%) of unsaturated dibromide fractions, b.p. 75–101° (0.4 mm.). A solid material formed in the fractions and was separated from the liquid in the same manner as that employed previously. After several recrystallizations from ethyl acetate, a total of 1.30 g. of *endo-cis*-5,6-dibromobicyclo[2.2.2]-oct-2-ene (XIX) was obtained, m.p. 147–148.5°. The infrared spectrum (CS_2) of XIX shows bands at 1233(m), 1205(m), 1170(w), 948(w), 935(w), 832(w), 797(w) and 712(s) cm.$^{-1}$.

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.12; H, 3.79; Br, 60.09. Found: C, 36.15; H, 3.85; Br, 60.40.

Concentration of the filtrate and mother liquors followed by distillation furnished the fractions

Fraction	B.p. °C.	B.p. Mm.	Wt., g.	n^{25}D
1	60–80	1	1	1.5591
2	80–81	1	2.22	1.5651
3	80–81	1	1.94	1.5651
4	80–85	0.5	3	1.5625

Fractions 2 and 3 were combined (4.16 g.) and taken as the liquid dibromide(s) from the reaction.

***cis*-2,3-Dibromobicyclo[2.2.2]octane (XVIII).**—A solution of 700 mg. (2.6 mmoles) of XIX in 15 ml. of ethyl acetate was hydrogenated in the presence of 80 mg. of prereduced platinum oxide. About 112% of the theoretical amount of hydrogen was taken up in 20 minutes. The solution was filtered and the filtrate was evaporated to dryness to yield a crystalline solid. Several recrystallizations from absolute methanol afforded 272 mg. of *cis*-2,3-dibromobicyclo[2.2.2]octane (XVIII), m.p. 79.5–81.0°. The infrared spectrum of XVIII (CS_2) is characterized by bands at 1200(s), 1137(m), 943(m) and 885(m) cm.$^{-1}$. Gas chromatography of XVIII on column B at 185° shows one peak with a retention time of 19.6 minutes. Under these same conditions the retention times of XVII and XX are 13.8 and 15.5 minutes, respectively.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.64. Found: C, 35.92; H, 4.59; Br, 59.66.

Hydrogenation of the Liquid Dibromide(s) from the Diels–Alder Reaction.—A 2.24-g. (8.4 mmoles) sample of the liquid dibromide(s) was hydrogenated in the manner described for the *endo-cis* isomer. The sample absorbed 87% of the theoretical amount of hydrogen. The catalyst was removed by filtration and the filtrate was concentrated. Distillation of the residue produced 1.19 g. of the saturated product, b.p. 95–100° (2 mm.), n^{25}D 1.5560. Gas chromatography indicated the presence of 49% XX, 37% XVII and 14% of an unknown dibromide.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectrum of *endo*-8-bromobicyclo[3.2.1]octane (VI) was measured[24a] on a Varian Associates high resolution spectrometer, V-4300B, using a 40-mc probe. The spectra for compounds VII and XV were obtained[24b] with a 60-mc probe. Carbon tetrachloride was used as the solvent. Chemical shifts were obtained by the side-band technique with tetramethylsilane as an internal standard.

Dipole Moment Determinations.—The dielectric constants were obtained using a commercial apparatus, previously described.[25] The moments were calculated by essentially the method of Halverstadt and Kumler[26] utilizing an IBM 650 computer.[27] Reagent grade benzene was used as the solvent. The dielectric constants and densities of the solutions of various mole fractions were measured at 25° and are listed in Table I.

TABLE I

DIPOLE MOMENT DATA

N_2	ϵ_{12}	d_{12}	
endo-8-Bromobicyclo[3.2.1]octane (VI)			
0.00924600	2.3286	0.880271	α 6.194, ϵ_{12} 2.2714
.00520051	2.3035	.877092	
.00432458	2.2985	.876455	β 0.772, d_1 0.87312
.00162929	2.2815	.874414	
.00000000	2.2713	.873100	$P_{2\infty}$ 132.0 cc. μ 2.089 ± 0.03 D.
endo-8-Bromobicyclo[3.2.1]oct-2-ene (VII)			
0.00553273	2.3088	0.877725	α 6.534, ϵ_{12} 2.2727
.00528709	2.3071	.877598	
.00251983	2.2894	.875303	β 0.802, d_1 0.87332
.00177886	2.2843	.874755	
.00000000	2.2726	.873328	$P_{2\infty}$ 135.4 cc. μ 2.13 ± 0.03 D.
trans-2,3-Dibromobicyclo[2.2.2]octane (XVII)			
0.00462590	2.3255	0.880600	α 10.976, ϵ_{12} 2.2749
.00365347	2.3152	.879105	
.00203636	2.2968	.876694	β 1.502, d_1 0.87364
.00092324	2.2855	.875088	
.00000000	2.2746	.873604	$P_{2\infty}$ 206.7 cc. μ 2.766 ± 0.03 D.
endo-cis-5,6-Dibromobicyclo[2.2.2]oct-2-ene (XIX)			
0.00191905	2.3033	0.876889	α 15.704, ϵ_{12} 2.2735
.00105480	2.2904	.875547	
.00084278	2.2870	.875197	β 1.543, d_1 0.87392
.00043809	2.2806	.874570	
.00000000	2.2731	.873944	$P_{2\infty}$ 274.2 cc. μ 3.313 ± 0.04 D.

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(24) (a) The spectrum was obtained through the courtesy of Dr. George Smith, General Motors Technology Center, Warren, Mich. (b) The spectra were determined by Professor G. J. Karabatsos, Department of Chemistry, Michigan State University.

(25) N. L. Allinger, H. M. Blatter, M. A. DaRooge and L. A. Freiberg, *J. Org. Chem.*, **26**, 2550 (1961).

(26) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(27) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

Radical Addition of Thiophenol to Bicyclo[2.2.2]oct-2-ene (III).—Employing a procedure similar to that of Cristol and Brindell,[28] an equimolar quantity of freshly distilled thiophenol was added to 4.0 g. (0.037 mole) of III. Distillation of the reaction mixture gave 5.53 g. (68%) of 2-thiophenylbicyclo[2.2.2]octane, b.p. 118–122° (0.8 mm.), n^{25}D 1.5859. A portion of this material was redistilled for analysis, b.p. 113.4–114° (0.6 mm.), n^{25}D 1.5851. The infrared spectrum (capillary) shows the following bands in the fingerprint region: 1270(m), 1200(w), 1093(m), 1067(w), 1027(m), 961(w), 742(s) (doublet) and 695(s) (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.00; H, 8.31; S, 14.69. Found: C, 77.25; H, 8.33; S, 14.91.

Desulfurization of 2-Thiophenylbicyclo[2.2.2]octane.—Approximately 5 g. of Raney nickel was added to a solution of the thioether (600 mg., 2.75 mmoles) in 40 ml. of 95% ethanol. The mixture was refluxed for 48 hr. The catalyst was removed by filtration and the filtrate was added to 300 ml. of water. This aqueous solution was then extracted with several portions of pentane and the combined extracts were washed with water, dried and concentrated by distillation. Sublimation of the residue afforded 124 mg. (41%) of bicyclo[2.2.2]octane, m.p. 166–168.5°, m.m.p. 166–169°. The infrared spectrum of this product shows none of the bands characteristic of bicyclo[3.2.1]octane.

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[28] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

The Conformations of Substituted Cyclopentanes. II. Maximally Puckered Envelope and Half-chair Models for Fused Ring Systems[1]

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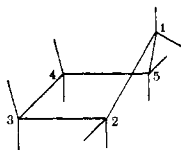
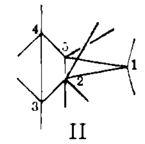
A pair of maximally puckered envelope and half-chair models ($\theta = 60°$) for use in the description of conformations of highly substituted and ring fused cyclopentanes is presented. Their bond bending energies (V_B), torsional energies (V_t) and electron correlation energies (London forces, E_c) have been calculated for comparison purposes. The use of these models in the estimation of the relative stabilities of the envelope and half-chair conformation of given molecules is discussed.

In a previous paper,[3] the two important conformations, the envelope (I) and half-chair (II) were described and applied to simply substituted, monocyclic cyclopentanes. In order to utilize these conformations in fused ring systems, however, models must be constructed in which the projected angle, $\theta_{1,2}$, sighted along C_1–C_2 in I or $\theta_{3,4}$ in II will be 60°.[4-6] The Pitzer and Donath model for cyclopentane itself has $\theta_{1,2} = \theta_{5,1} = 46.1°$ for the envelope conformation and $\theta_{3,4} = 48.1°$ for the half-chair.[4] Further, our earlier model for cyclopentanone was mainly concerned with the projected angle between the carbonyl group and the α-substituent.[3] In this paper, we have constructed through vector analytical techniques[4,7,8] a pair of maximally puckered models of general applicability to fused rings and highly substituted cyclopentanes.

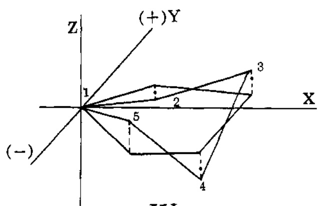


I

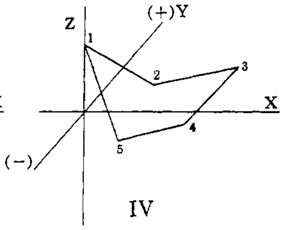


II

We begin with a planar, five-membered ring located in a coördinate system as shown below (III). The amplitude of puckering (q)[4,9] was allowed to increase until the torsional angles (θ's) had in each form reached the desired values. The interior angles of the ring (ω_i) and torsional angles (θ_{ij}) for the resulting, symmetrical models are given in Table I.[10]



III



IV

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[1] Previous communication in this series, F. V. Brutcher, Jr., and William Bauer, Jr., *Science*, **132**, 1489 (1960). The material in this paper and the following one on ring D in the steroids was presented at the Autumn Meeting of the National Academy of Sciences held at the University of Pennsylvania on November 14, 1960.

[2] Armstrong Cork Co. Predoctoral Fellow 1960–1961.

[3] F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

[4] K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).

[5] Inspection of scale models of steroid rings C and D built according to the reported X-ray analyses of several steroid systemsi ndicates that this is approximately the case.[6] The much more complicated fused ring cases, where θ may not be equal to 60°, are under consideration in this Laboratory.

[6] (a) C. H. Carlisle and D. Crowfoot, *Proc. Royal Soc. (London)*, **184A**, 81 (1945); (b) D. Crowfoot, Hodgkin and D. Sayre, *J. Chem. Soc.*, 4561 (1952); (c) R. G. Curtis, J. Friedrichsons and A. McL. Mathieson, *Nature*, **170**, 321 (1952); *J. Chem. Soc.*, 2159 (1953).

[7] The treatment involves the assumption that the angles $\omega_2 = \omega_5$ are also equal to ω_1. This assumption, which makes the calculations tractable; was found by Kilpatrick, Pitzer and Spitzer[8] to give substantially the lowest energy.

[8] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 211 (1947).

[9] It is important to note that q in Å., which is a *measure* of the amplitude of puckering, is *not* the distance of carbon 1 in the envelope out of the C_2–C_3–C_4–C_5 plane. We have transformed q for cyclopentane itself and also for our maximally puckered models to the following numbers which are more meaningful for organic chemists. In cyclopentane itself the C_1 distance (envelope) from the C_2–C_3–C_4–C_5 plane is 0.75 Å.; in our maximally puckered model it is 0.91 Å. For the half-chair with C_2–C_1–C_5 the reference plane, C_3 in cyclopentane itself is 0.39 Å. above the reference plane while C_4 is equally below the plane. In our maximally puckered model (half-chair) C_3 is 0.48 Å. above and C_4 is 0.48 Å. below the C_2–C_1–C_5 plane. It also might be pointed out that q is not needed for vector analytical work on organic molecules (*e.g.*, for cyclohexene see E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1954) and for bicycloheptane, C. F. Wilcox, *ibid.*, **82**, 414 (1960)). The technique involving q is derived from vibrational methods of analysis such as those used for pseudorotating molecules such as cyclopentane.[8]

[10] It is useful to note that when a cyclopentane ring adopts either the envelope or half-chair *all* interior angles turn out to be *less* than the tetrahedral value of 109° 28'.