syn-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-ol (m.p. 137.5–138.5°) (X) was depressed. The infrared solution spectra of the two compounds taken in carbon disulfide showed marked differences.[4]

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.08. Found: C, 75.02; H, 5.07.

syn-8-**Chlorodibenzobicyclo[3.2.1]octadien**-*endo*-**2-yl Acetate (VIII)**.—A solution of 263 mg. (1.025 mmoles) of VII in acetic anhydride and several drops of concentrated sulfuric acid was heated on a hot plate for 5 min. The solution was poured slowly into water and extracted with two 50-ml. portions of chloroform. The reaction mixture was dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The oily residue was dissolved in carbon tetrachloride and subjected to column chromatography on a column which was packed with 100 g. of Woelm neutral alumina in carbon tetrachloride. The column was eluted with the following solvents: carbon tetrachloride, chloroform, and 10% ethyl acetate in chloroform. The first fraction containing ethyl acetate yielded 253 mg. (83%) of VIII melting at 133.5–138°. Recrystallization from ethanol gave a melting point of 136–137°.

This compound when compared with IV showed different infrared solution spectra in carbon disulfide. A mixture melting point for the two isomers was depressed.

An analysis was obtained in this laboratory[9] for a compound believed to be the *syn*-chloro-*endo*-acetate, but synthesized in a different manner. This melted at 145–146°. When a mixture melting point was taken of the two, the mixture melted at 138.5–141.5°. A remelting point of the resolidified mixture was 135–136.7°. There was a marked difference between the infrared spectra of the two compounds from 13–25 μ when the spectra were taken in potassium bromide pellets. When the two samples were each dissolved in carbon disulfide, their solution spectra were shown to be identical from 2–25 μ. Crystalline modifications were observed both in the *syn*-chloro-*endo*-alcohols and acetates. Products from the [3.2.1] ring system were always compared in the above manner.

The Permanganate Oxidation of *syn*-8-**Chlorodibenzobicyclo[3.2.1]octadien**-*endo*-**2-ol (VII) to** *syn*-8-**Chlorodibenzobicyclo[3.2.1]octadien-2-one (IX)**.—Compound VII (149 mg., 0.580 mmole) was subjected to the permanganate oxidation procedure previously reported for the *syn*-8-chloro-*exo*-2-alcohol.[2] The product, 130 mg. (87%) of a white crystalline compound, showed a melting point of 121–122°. A mixture melting point with known *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-2-one (IX)[2] showed no depression. Infrared spectra of both samples were identical.

The Epimerization of *syn*-8-**Chlorodibenzobicyclo[3.2.1]octadien**-*exo*-**2-yl Acetate (IV) to** *syn*-8-**Chlorodibenzobicyclo[3.2.1]octadien**-*endo*-**2-yl Acetate (VIII)**.—A mixture of 1.54 g. of 70% perchloric acid (1.54 mmoles), 10 ml. of glacial acetic acid, and 438 mg. (1.46 mmoles) of IV was heated at 85° for 4 hr. The solution was then poured into 200 ml. of water and extracted with two 100-ml. portions of benzene. The organic layer was washed with a 5% sodium bicarbonate solution and then twice with water. The benzene extract was then dried over anhydrous sodium sulfate, filtered, and the solvent was removed by rotary evaporation, leaving 432 mg. of a clear yellow oil. A spectrum of the crude product was identical with that of the *endo*-acetate VIII. The product was recrystallized from petroleum ether (b.p. 60–70°) twice, and 114 mg. of a compound melting at 141–142° was obtained. A mixture melting point with a sample of VIII showed no depression. A solution spectrum of the product in carbon disulfide was taken from 2–25 μ and was found to be identical with that of VIII.

The mother liquors from the recrystallizations were combined and subjected to elution chromatography on an alumina column packed with 10 g. of Woelm neutral alumina. The chromatogram was eluted with petroleum ether (b.p. 60–70°), carbon tetrachloride, and chloroform. The fractions eluted with chloroform (217 mg.) yielded upon recrystallization 120 mg. of a compound melting at 121–139° and having a solution spectrum identical with that of VIII. The impurity seemed, from the crude infrared spectrum, to be a small amount of the hydrolysis product *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*endo*-2-ol (VII). When the mother liquors were combined and the solvent removed by rotary evaporation, an oil weighing 23 mg. was obtained. The oily product was dissolved in 10 ml. of acetic anhydride, and 2 drops of concentrated sulfuric acid was added. The mixture was warmed for several minutes and then poured slowly into water. The aqueous mixture was extracted twice with benzene, and the combined organic layers were decolorized with Norit and dried over anhydrous sodium sulfate. When the solvent was removed by rotary evaporation, 27 mg. of a compound having a melting point of 121–135° was obtained. Upon recrystallization from petroleum ether (b.p. 60–70°), 15 mg. of a compound, m.p. 128–140°, was recovered. An infrared spectrum of this compound showed it to be VIII. The crude yield of VIII was 58%.

Dipole Moments, Configuration, and Conformation of Tricyclo[5.1.0.0³,⁵]octane Derivatives and Related Compounds[1]

BY W. D. KUMLER, ROBERT BOIKESS, P. BRUCK, AND S. WINSTEIN

Tricyclo[5.1.0.0³,⁵]octane (VI), 4,4-dibromotricyclo[5.1.0.0³,⁵]octane (V), and 4,4,8,8-tetrabromotricyclo[5.1.0.0³,⁵]octane (III) have been prepared. The dipole moments of these compounds as well as those of norcarane (VIII), Δ³-norcarene (IV), 7,7-dibromobicyclo[4.1.0]heptane (VII), Δ³-7,7-dibromobicyclo[4.1.0]heptene (II), 1,4-cyclohexadiene (I), cyclohexene, and cyclopentene have been measured. Zero dipole moment for III proves its configuration is *trans* and the six-membered ring has a relatively flat conformation. The methods of preparation indicate a *trans* configuration for VI and V and the dipole moment values favor nearly flat conformations for the six-membered rings in these compounds. Cyclohexene and cyclopentene were found to have dipole moments of 0.21 D. which are considerably smaller than most values in the literature. Norcarane has a moment of 0.44 D. The evidence indicates the central ring is relatively flat when either cyclopropane or olefinic groups are on opposite sides of a six-membered ring.

In the course of another study[2] it was necessary to determine the configurations of the bismethylene adducts (VI) of 1,4-cyclohexadiene (I). One of the bis-

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962; Abstracts, p. 80Q.

(2) P. Bruck and R. Boikess, unpublished work.

adducts can be derived from the crystalline tetrabromide[3] III, the bisdibromocarbene adduct of 1,4-cyclohexadiene. As a guide to configuration, the dipole moment of the tetrabromide was determined, and in

(3) (a) K. Hofmann, *et al.*, *J. Am. Chem. Soc.*, **81**, 992 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).
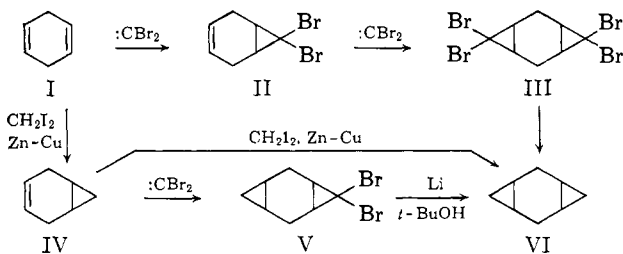
TABLE I

SUMMARY OF DIPOLE MOMENTS AND RELATED DATA

	ϵ_1	ν_1	α	β	p_{2_0}	P_{2_0}	P_{E_2}	μ	Est. at. polariz., μ	
III, *trans*	2.27382^d	1.13891	0.21233	−0.69932	0.17074	72.36	60.24^a 65.00^b	0.77	12.1	0.0
VII	2.27217^d	1.14122	2.21213	− .58781	.57975	141.43	43.79^a 45.62^b	2.19 ± 0.01	6.0	2.12 ± 0.01
VIII	1.91754^e	1.47043	0.32162	− .28750	.36950	35.54	30.86^a 30.79^b	0.48	0.8	0.44
V, *trans*	2.27479^d	1.14151	1.94731	− .60149	.52597	139.91	47.14^a 49.46^b	2.13 ± 0.01	6.0	2.07 ± 0.01
VI, *trans*	1.91789^e	1.46772	0.23940	− .40788	.31697	34.29	32.97^a 32.22^b 33.14^c	0.25	1.0	0.13
	1.91768^e	1.46881	.35116	− .22154	.35116	28.84	27.21^e 27.20^b 27.03^c	.28	0.7	.21
	1.92042^e	1.46778	.13956	− .17321	.34392	23.42	22.11^a 21.59^b 22.13^c	.25	0.4	.21
I	1.91738^e	1.46900	.24472	− .28891	.34664	27.77	26.14^a 26.77^b 26.14^c	.28	1.2	.13
IV	1.91799^e	1.46889	.34798	− .36829	.35997	33.68	29.30^a 30.33^b 29.52^c	.46	1.1	.40
II	2.27199^d	1.13448	1.79543	− .58183	.49928	120.75	44.35^a 44.83^b	1.93 ± 0.01	6.0	1.87 ± 0.01

ϵ_1, dielectric constant; ν_1, specific volume; α, slope of $\epsilon_{12} - \omega_2$ plot; β, slope of $\nu_{12} - \omega_2$ plot; p_{2_0}, specific polarization; P_{2_0}, molecular polarization; P_{E_2}, electronic polarization; μ, dipole moment; ω, weight fraction.

[a] From refractive index of solution. [b] From atomic refractions. [c] From refractive index of pure liquid. [d] Measured in benzene at 25°. [e] Measured in heptane at 25°.

the course of this work measurements were made on a number of related compounds and still other materials for comparison. The results of this study are presented and discussed in the present article.

Results

The dipole moment values in Debye units and other data are given in Table I.

All values were obtained using the Halverstadt–Kumler equation and method of calculation.[4] Mo-

$$p_{2_0} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + (\nu_1 + \beta)\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

ments were calculated using an IBM 1620 computer. In case of the compounds with dipole moments above 1.5 D., the accuracy of the determinations as indicated by the scatter of points on the $\epsilon_{12} - \omega_2$ line was within 0.01 to 0.02 D. The accuracy with compounds with moments less than 0.5 D. is less and here the atomic polarization is a limiting factor and this has been estimated in each case usually by comparison of the atomic polarization of analogous compounds.

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

Dipole Moments, Configuration, and Conformation.— The pure crystalline tetrabromide III, m.p. 204–206°, gave a P_{2_0} value of 72.36 and a P_{E_2} value of 60.24 from the refractive index of the solutions. A dipole moment of 0.77 D. is calculated making no allowance for atomic polarization. From atomic polarization values of 3 for ethyl bromide, 6.1 for *p*-dibromobenzene, and 6.2 for *trans*-1,4-dibromocyclohexane,[5] an atomic polarization value of 12 may be estimated for tetrabromide III. On this basis, the derived dipole moment for III is zero.

The vanishingly small value of the dipole moment of III proves that this compound has the two cyclopropane rings in a *trans* rather than *cis* relationship. This may be seen more clearly by examining dipole moment values estimated for different conformations of both *cis* and *trans* isomers of III. To make these estimates it is helpful to consider the dipole moments of 7,7-dibromonorcarane[6] (VII) and norcarane (VIII) itself.

The direction of the dipole between the six-membered and the three-membered ring in norcarane structural types is of concern in calculating the theoretical dipole moment of the different conformations of compounds discussed in this paper. The angle to be considered is that between the direction of this dipole and the plane of the three-membered ring. One extreme possibility is that the dipole between the two rings is in the plane of the bonds between the CH_2 carbons in the six-membered ring attached to the carbons common to both rings. This gives an angle of 75° between it and the plane of the cyclopropane ring. The other extreme is that the dipole is along the line connecting the centers

(5) W. Kevestrov, F. A. Meijer, and E. Havinga, *Rec. trav. chim.*, **T73**, 718 (1954).

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

TABLE II

CONFIGURATIONS, CONFORMATIONS, AND CALCULATED DIPOLE MOMENTS

	Configuration	Conformation six-membered ring	Angle between dipoles	Dipole moment Calcd.	Obsd.
	III	*trans* Boat	154°	0.95	
	III	*trans* Flat	180°	0.0	
	III	*cis* *cis*-Boat	9°	4.20	0.0
	III	*cis* *trans*-Boat	109°	2.76	
	III	*cis* Flat	59°	3.65	
	VI	*trans* Boat	130°	0.37	
	VI	*trans* Flat	180°	0.0	0.13
	V	*trans* Boat-Br *trans*	172°	1.67	
	V	*trans* Boat-Br *cis*	172°	1.67	2.07
	V	*trans* Flat	122°	1.92	
	IV	*cis*-Boat	130°	0.35	
	IV	*trans*-Boat	145°	0.30	0.40
	IV	Flat	175°	0.23	
	II	*cis*-Boat	77°	2.17	
	II	*trans*-Boat	157°	1.92	1.87
	II	Flat	117°	2.02	
	I	Boat	135°	0.16	0.13
	1	Flat	180°	0.0	

of the two rings which gives an angle of 50° between it and the plane of the cyclopropane ring. It is likely that the dipole is in a direction in between these two extremes and one can get an indication of where it is by considering 7,7-dibromonorcarane (VII).

For 7,7-dibromonorcarane (VII) the P_{2_0} of 141.43 and a P_{E_2} of 43.79 from the refractive index of the solutions give a moment of 2.19 D. neglecting atomic polarization. Assuming an atomic polarization of 6, the moment is calculated to be 2.12 D. It is clear that the resultant of the two C–Br dipoles in this compound must be in the plane of the three-membered ring. This resultant is calculated taking the value of the C–Br dipole as the moment of bromocyclopropane,[7] 1.7 D. (1.69 D.), and the angle between the C–Br dipoles as 112°, the same as that between the C–Cl dipoles in

1,1-dichlorocyclopropane.[8] This gives a resultant of 1.91 D. and it will be in the plane of the cyclopropane ring. Using the moment of norcarane (VIII) of 0.44 D. as the moment of the dipole between the six- and the three-membered ring, it is found that this must make an angle of 69° with the direction of the resultant of the C–Br dipoles to give the observed moment of 2.12 D. The direction of this dipole is in between the two extreme situations as was anticipated.

Norcarane was found to have a P_{2_0} of 35.54 and a P_{E_2} of 30.86 from solution measurements which gave a dipole moment of 0.48 D. If one assumes an atomic polarization of 0.8, the dipole moment is 0.44 D.

The direction the resultant dipole of 7,7-dibromonorcarane makes with the plane of the cyclopropane ring is 12° from the plane of the ring on the opposite side from the six-membered ring.

With these values the theoretical moments of the different conformations of both the *cis* and *trans* configurations of the tetrabromo compound III and other norcarane derivatives can be calculated. In Table II are given the calculated dipole moments for the various configurations and conformations of the norcarane derivatives. Included also is the angle between the principal resultant dipoles in each of the different conformations.

Considering both boat and flat conformations of the six-membered ring in the tetrabromide III, it is obvious that the *cis* configuration can be ruled out immediately because high dipole moments are expected for any of the conformations.

On the other hand, the observed dipole moment of the tetrabromide III is quite consistent with the *trans* configuration. Since dipole moments of 0.95 and 0.0 are estimated for ordinary boat and flat conformations, respectively, the observed moment of zero for III supports a relatively flat conformation.

The proof of *trans* configuration for III also constitutes proof of *trans* configuration for the bismethylene adduct VI obtained by lithium debromination of III. Similarly, the dibromide V, obtained by the addition of dibromocarbene to norcarene (IV), is proved to be *trans* since it yields the pure *trans*-VI on lithium debromination.

The bis-adduct VI may also be prepared from 1,4-cyclohexadiene (I)[2,9] by the Simmons–Smith reaction employing a large excess of methylene iodide and zinc–copper couple or by the use of diazomethane and cuprous chloride.[10] These methods lead to mixtures of *cis* and *trans* isomers,[2,9,10] and comparison of infrared spectra shows the *trans* compound examined in the present work to be identical with the major bis-adduct produced in these reactions.

The *trans* assignment to the bis-adduct VI encountered in the present work is confirmed by nuclear magnetic resonance spectroscopy.[11,12] In *trans*-VI each of the alicyclic methylene protons is *cis* to one cyclopropane ring and *trans* to another and thus all four protons have the same average magnetic environment. Therefore, only one alicyclic methylene proton signal is observed. On the other hand, the *cis*-VI,

(7) J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

(8) J. M. O'Gorrman and V. Schomaker, *ibid.*, **68**, 1138 (1946).

(9) H. Simmons, private communication.

(10) W. von E. Doering, private communication.

(11) R. S. Boikess, J. I. Brauman, and S. Winstein, unpublished work.

(12) See R. S. Boikess and S. Winstein, *ibid.*, **85**, 343 (1963).

obtained in another investigation,[2,12] has two methylene protons *cis* to two cyclopropane rings and two protons *trans* to the cyclopropane rings. Thus it has two types of methylene protons and therefore gives rise to two alicyclic methylene proton signals.

The dipole moment of the *trans*-bis-adduct VI and the related dibromide V were determined in the present work (Table I). For VI, the observed value of 0.13 D. points to a relatively flat conformation, since the calculated value for the boat conformation (Table II) is 0.37 D. and that for the flat conformation is zero. For the dibromide V, the flat conformation is again somewhat favored since the observed value of 2.07 D. is closer to the value of 1.92 estimated for the flat conformation than to 1.67 estimated for the boat.

Other Compounds.—In the course of the present work it seemed advisable to determine the dipole moments of cyclohexene and cyclopentene. As summarized in Table I, the dipole moment values of each compound is 0.21 D. For 1,4-cyclohexadiene (I), a dipole moment value of 0.13 D. was obtained, while for norcarene (IV) the value is 0.40 D. (Table I). For the 7,7-dibromonorcarene[3] (II), the value obtained is 1.87 D. For each of the cases an estimated value of the atomic polarization was employed (Table I) based on analogy with values for other compounds listed by Smyth.[13]

The dipole moment values for cyclohexene and cyclopentene obtained in the present work are considerably lower than the values of 0.75, 0.63, and 0.61 previously reported for cyclohexene,[14] and 0.97 and 0.92 reported for cyclopentene.[14] However, there is one paper[15] which gives a value of 0.28 D. for the moment of cyclohexene and this is in essential agreement with our value of 0.21 D. Our present values are more in keeping with the literature values of 0.35 for propylene[14] and 0.30 and 0.37 for butene.[14] Comparing the dipole moment values for cyclohexene and norcarane (VIII), the indications from the present work are that a cyclopropane ring gives rise to a larger moment than does an olefinic group. It would be of obvious interest to have other comparisons of this same kind.

Another interesting observation of the present work on the cyclopropane-ring-containing compounds is that the electronic polarization values (P_{E_2}) determined from the refractive index of the actual solutions of the bromo compounds III, VII, V, and II are all lower than the values (MR_D) based on atomic refractions. In the case of the tetrabromide III, the discrepancy is 4.76, while with V and VII it is 2.32 and 1.83, respectively. This observation is in keeping with the general principle that electrons are held more tightly in s- than in p-orbitals and the more s- character in a hybrid orbital, the more tightly the electrons will be held. This applies both to electrons in bonds attached to the atom under consideration, and to lone pair electrons on atoms attached to this atom. An example of the first is the fact that the C–H group where C is aromatic has a refraction of 1.40, while a C–H group where C is aliphatic has a refraction of 1.70.[16] An example of the second is

that fluorine atoms in *sym-cis*-difluorodichloroethylene have a refraction of 0.99, while fluorine in *sym*-tetrafluorodichloroethane has a value of 1.223.[17] With cyclopropane compounds the carbon atoms in the cyclopropane rings have more s- character in the bonds to bromine atoms and the refraction of the compounds might be expected to be low as is actually observed.

Conformation.—For norcarene, a conventional half-chair conformation of the six-membered ring may be visualized and this is proved[11] by its nuclear magnetic resonance spectrum in the region for methylene protons vicinal to the cyclopropane ring, which eliminates *cis*- and *trans*-boat modifications from consideration.

In the case of tetrabromide III, dibromide V, and *trans*-bis-adduct VI discussed earlier, the dipole moment evidence favored a relatively flat conformation of the middle six-membered ring. With 1,4-cyclohexadiene (I), norcarene (IV), and dibromonorcarene II, the dipole moment evidence provides very little assistance as regards conformation. As is clear from Table II, it is not possible to decide between flat or boat conformations of the six-membered ring in these compounds on the basis of the observed moments. For *trans*-VI and norcarene (IV), the nuclear magnetic resonance spectra[11] in the alicyclic methylene proton region are consistent with either a flat or boat conformation for VI and either a flat or *cis*-boat conformation for norcarene. In the latter case, a *trans*-boat conformation is ruled out. For both *trans*-VI and norcarene, inspection of models suggests the flat conformation would be preferable on the basis of greater nonbonded repulsions in the boat modifications.

For 1,4-cyclohexadiene, Gerding and Haak,[18] from an investigation of Raman and infrared spectra, concluded that the molecule is nearly flat. Thus the overall picture favors a relatively flat central ring when cyclopropane or olefinic groups are on opposite sides of a six-membered ring.

There are three effects that tend to favor flatness in these six-membered rings. The increased s- character in bonds *exo* to a three-membered ring and the presence of sp^2 carbons in the double bond increases four angles in the six-membered ring, which tends to flatten the ring. The opposition of hydrogens in the boat are relieved by the flatness. The state of lowest energy as far as dipole interactions are concerned occurs when the dipoles are directly opposed, which is the situation when the six-membered ring is flat.

Experimental

1,4-Cyclohexadiene was prepared by the reduction of benzene with sodium in liquid ammonia. Purification was effected by two preparative vapor phase chromatographic passes, collecting only peak centers, followed by distillation under anhydrous conditions. Clear, colorless liquid, n^{25}D 1.4678 (reported[19] n^{20}_{5893} 1.4275), was obtained.

Norcarane was prepared by the reaction of zinc–copper couple, methylene iodide, and cyclohexene using a modification[20] of the procedure of Smith and Simmons.[21] Purification was effected by two preparative vapor phase chromatographic passes, collecting only the peak centers, followed by distillation from calcium hydride under anhydrous conditions. Clear colorless liquid, b.p. 116–117° (749 mm.) (reported[21] 116–117°), n^{25}D 1.4539 (reported[21] n^{25}D 1.4546), was obtained.

(13) C. P. Smyth, "Dielectric Behavior and Structure," McGraw–Hill Book Co., Inc., New York, N. Y., 1955, p. 420.

(14) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

(15) A. P. Altshuller, *J. Phys. Chem.*, **59**, 32 (1955).

(16) Reference 13, p. 409.

(17) "Landolt-Bornstein," 5th Ed., 3rd Suppl., 2nd part, p. 1695.

(18) H. Gerding and F. A. Haak, *Rec. trav. chim.*, **68**, 293 (1949).

(19) J. P. Wibaut and F. A. Haak, *ibid.*, **67**, 85 (1948).

(20) R. S. Boikess and E. C. Friedrich, unpublished work.

(21) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

Δ³-**Norcarene.**—The reaction of 1,4-cyclohexadiene, methylene iodide, and zinc–copper couple, run by a modification of the procedure of Smith and Simmons,[21] afforded Δ³-norcarene, b.p. 114–116° (reported[3b] 115–115.5°), $n^{25.0}$D 1.4740 (reported[3b] 1.4740), in 37% yield. Purification was effected by two preparative vapor phase chromatographic passes, collecting only peak centers, followed by distillation from calcium hydride under anhydrous conditions. Clear colorless liquid, b.p. 114.5–115.0° (749 mm.), n^{25}D 1.4732, was obtained. This material has also been prepared by this same method by Simmons.[9]

7,7-Dibromobicyclo[4.1.0]heptane was obtained by the reaction of dibromocarbene with cyclohexene.[6] Fractionation of the product, followed by refractionation of a center cut, gave clear colorless liquid, b.p. 87.5–88.0° (5 mm.), n^{23}D 1.5527. We are indebted to Mr. Phillip Radlick for preparation of this compound.

Δ³-**7,7-Dibromobicyclo[4.1.0]heptene** was prepared as previously described.[3b] Recrystallization from ethanol afforded a sample, m.p. 37–38° (reported[3b] 37.8–38.8°).

4,4-Dibromotricyclo[5.1.0.0³,⁵]octane.—To a stirred solution, maintained under anhydrous conditions and a nitrogen atmosphere, of 9.4 g. (0.1 mole) of Δ³-norcarene and 37.95 g. (0.15 mole) of bromoform, freshly distilled from mercury, in 50 ml. of t-butyl alcohol, distilled from calcium hydride, was added dropwise over 2 hr. 22.4 g. of potassium t-butoxide in 200 ml. of anhydrous t-butyl alcohol. The mixture was stirred for 9 hr. and then poured into 500 ml. of pentane and 100 ml. of water. The pentane was extracted with five 100-ml. portions of water, dried over anhydrous sodium sulfate, and, after filtration, the pentane was evaporated on a steam bath through a Vigreux column. The residue was pumped at 25° (30 mm.) for 6 hr. Distillation afforded a middle cut of 4.54 g. (17%), b.p. 84–85° (3 mm.), n^{25}D 1.5631. Redistillation and collection of a middle cut gave clear colorless liquid, b.p. 73.5–74.0° (1.5 mm.), n^{25}D 1.5651.

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.12; H, 3.79; Br, 60.01. Found: C, 36.20; H, 3.99; Br, 60.25.

A solution of 1.06 g. of the dibromide, n^{25}D 1.5631, and 3.5 g. of t-butyl alcohol in 30 ml. of tetrahydrofuran, purified by contact with potassium hydroxide pellets for 3 days and then distillation from lithium aluminum hydride, was stirred under a stream of argon while 0.66 g. of lithium wire was cut in the neck of the flask with a long point scissors. The reaction began immediately and stirring under anhydrous conditions was continued for 3 hr. The mixture was then poured into ice–water through a glass wool plug. The water was extracted with three 100-ml. portions of pentane and the pentane extracted with five 50-ml. portions of water and dried over anhydrous potassium carbonate. Vapor phase chromatography indicated that 99.3% of the hydrocarbon was the *trans* isomer, while 0.7% was the *cis* isomer.[2]

4,4,8,8-Tetrabromotricyclo[5.1.0.0³,⁵]octane was prepared as previously reported.[3b] Two recrystallizations from chloroform gave thick needles, m.p. 204.2–206.2° (reported[3b] 205–206°).

Anal. Calcd. for $C_8H_8Br_4$: C, 22.46; H, 1.90; Br, 75.42. Found: C, 22.54; H, 1.82; Br, 75.21.

Tricyclo[5.1.0.0³,⁵]octane.—Dehalogenation of 1.57 g. of the tetrabromide with lithium and t-butyl alcohol in tetrahydrofuran afforded after distillation 0.2 g. of a hydrocarbon which had no (<0.1%) *cis* isomer detectable by vapor phase chromatography. Purification was effected by preparative vapor phase chromatography in the same manner as above, followed by distillation from calcium hydride under anhydrous conditions. Clear colorless liquid, n^{25}D 1.4760, b.p. (micro) 140.6° (749.6 mm.), was obtained.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.52; H, 11.05.

The infrared spectrum of this product was identical with that of the major bis-adduct obtained by Simmons[9] and also Boikess[2] from the Simmons–Smith reaction on 1,4-cyclohexadiene. It was also identical with the spectrum of the predominant bis-adduct obtained by Doering[10] using diazomethane–cuprous chloride.

Cyclohexene.—Eastman cyclohexene was distilled from sodium through a Todd column; the fraction boiling at 83° at 759 mm. was used.

Cyclopentene.—Aldrich cyclopentene was distilled from sodium through a Todd column; the fraction boiling at 45° at 759 mm. was used.


A Nuclear Magnetic Resonance Study of the Products from an Unusual Reaction of Norbornadiene. The Ionic Addition of N-Chlorodiethylamine in Sulfuric Acid–Acetic Acid

BY ROBERT S. NEALE AND EARL B. WHIPPLE

The reaction between N-chlorodiethylamine and norbornadiene in acetic acid 4 M in sulfuric acid and 1.5 M in water, under either nitrogen or air, yielded 30% of two 1:1 adducts, exo-2-diethylamino-syn-7-chloro-5-norbornene (III) and a single isomer of 3-chloro-5-diethylaminonortricyclene (IV). Also isolated was 30% of a mixture of three isomeric derivatives of norbornadiene bearing chlorine and acetoxy substituents. An ionic pathway rather than the expected radical pathway to the basic products III and IV is indicated from the stereochemistry of III and from the insensitivity of the balance between neutral and basic products to the presence of air. It is therefore remarkable to have obtained a fair yield of *basic* products in a medium acidic enough to have completely protonated all the bases present. The carbonium ion resulting from exo addition of Cl⁻ to norbornadiene appears to be the precursor common to all five reaction products. It was possible to deduce completely the stereochemistry of III and two of the three nortricyclene-type products solely on the basis of their n.m.r. spectra.

In a previous paper[1] it was reported that N-chlorodialkylamines undergo free radical addition to butadiene to afford products of 1,4-chloroamination (eq. 1), but that 1,1-diphenylethylene yields only the ionically-derived product 1-chloro-2,2-diphenylethylene under identical conditions. Norbornadiene was also

$$R_2NCl + CH_2=CHCH=CH_2 \xrightarrow[\text{HOAc, } N_2]{\text{H}_2\text{SO}_4} R_2NCH_2CH=CHCH_2Cl \quad (1)$$
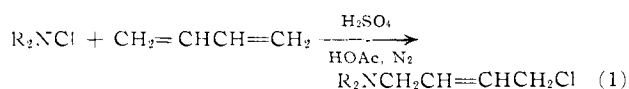
employed as the olefinic substrate[1] to determine whether the expected anchimeric participation[2] of one double bond might result in radical addition of the chloroamine similar to that observed for butadiene, or whether ionic chlorination might occur instead. The experiment was one of several designed to test the effect of an olefin's structure upon its ability to undergo a chloroamination reaction, a topic presently under active study. Although both neutral and basic products were formed in the reaction between norbornadiene and N-chlorodiethylamine, only ionic processes

(1) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

(2) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).