[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

The Stereochemistry of Additions to Olefins. I. The Free Radical Addition of Hydrogen Bromide to 2-Bromo-2-norbornene[1]

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The Diels–Alder reaction of cyclopentadiene and dibromoethylene gave a mixture of *trans*-5,6-dibromo-2-norbornene and *exo-cis*-5,6-dibromo-2-norbornene. Only small amounts of the expected *endo-cis* isomer could be obtained. The unsaturated dibromides were hydrogenated to give the corresponding norbornane derivatives. The assignments of configuration of these compounds were based on: (1) dehydrobromination of the saturated dibromides to 2-bromo-2-norbornene and (2) dipole moment measurements. The ultraviolet light initiated addition of hydrogen bromide to 2-bromo-2-norbornene produced a mixture of *trans*-2,3-dibromonorbornane (III) and *exo-cis*-2,3-dibromonorbornane (V). These products were not interconverted under the reaction conditions. Since ionic addition was completely suppressed, formation of the *exo-cis* isomer represents a *trans* radical addition to a norbornylene. *exo*-2-Norbornyl bromide (VIII) was also detected and its mode of formation is discussed.

In connection with other studies being carried out in this Laboratory a synthetic route to *exo-cis*-2,3-dibromonorbornane (V) was desired. The Diels–Alder addition of *cis*-1,2-dibromoethylene to cyclopentadiene followed by hydrogenation of the adduct was considered only a remote possibility because of the numerous reports of the formation of predominantly *endo* products in such reactions. A pertinent example is the formation of *endo-cis*-5,6-dichloro-2-norbornene from cyclopentadiene and *cis*-1,2-dichloroethylene.[2] Among other synthetic approaches, the free radical addition of hydrogen bromide to 2-bromo-2-norbornene (I) seemed to offer a good possibility.

The elegant studies of Goering and co-workers have convincingly demonstrated a stereospecific *trans* process for the radical addition of hydrogen bromide to several simple alicyclic[3a,b] and more recently acyclic olefins.[3c] However, a strong preference for *exo-cis* radical additions to the norbornylene system has been observed. These cases include: the brominations (presumably homolytic) of the maleic anhydride adducts of furan and cyclopentadiene[4a,b]; the addition of ethyl bromoacetate to norbornylene[5]; and the addition of the thiyl radical to 6-chloro-aldrin.[6] An apparent exception to this orientation is the reported *trans* addition of bromotrichloromethane to norbornylene,[7] but reinvestigation has shown that the *exo-cis* compound is the exclusive product.[8] As opposed to these relatively slow reactions, the high reactivity between olefins and hydrogen bromide led us to expect, at worst, a mixture of V and the *trans* isomer III from the addition of hydrogen bromide to I.

The route outlined below was employed for the preparation of the vinyl bromide I. Cyclopentadiene and a mixture of *cis*- and *trans*-1,2-dibromoethylene in a steel bomb at 185° for four hours formed 14–20% of *trans*-5,6-dibromo-2-norbornene (II) and 6–8% of a solid adduct. The configuration of the *trans* isomer was established by hydrogenation to the saturated dibromide III, which had identical physical properties and infrared spectrum with the known *trans*-2,3-dibromonorbornane.[9] When III was heated with potassium *t*-butoxide in *t*-butyl alcohol 2-bromo-2-norbornene (I) was obtained in 74% yield.

Further characterization of the solid dibromide led, unexpectedly, to its assignment as *exo-cis*-5,6-dibromo-2-norbornene (IV). Hydrogenation of IV over platinum oxide resulted in a quantitative yield of *exo-cis*-2,3-dibromonorbornane (V). The dehydrobromination of V also produced I in good yield demonstrating that the halogen substituents were located at C_2 and C_3 of the bicyclic nucleus (the 2,2-isomer is eliminated by the dipole moment).

The conclusive evidence for the *exo-cis* configuration of IV (and V), excluding the hydrogen bromide addition studies which will be discussed below, resides in the dipole moment measurements. A theoretical dipole moment of 3.61 D., calculated by assuming tetrahedral angles at C_2 and C_3 and selecting a value of 1.91 D.[10] to describe the carbon–bromine bond moment, was obtained for V (the same value should also apply to the *endo-cis* isomer VII). In order to derive a satisfactory value for the unsaturated *exo-cis* compound IV, a contribution of 0.40 D. was assigned to the strained 2,3-olefinic bond.[11] The C_2–C_1–C_6 angle was taken as ~100°.[12] The over-all symmetry of IV requires an angle of ~160° between the opposing group moments ($\mu_{C_5Br\ +\ C_6Br}$; $\mu_{C_2=C_3}$) and leads to a calculated theoretical moment of 3.24 D. The observed moments of IV and V, measured in benzene solution, were found to be 2.97 and 3.21 D., respectively. The agreement with the theoretical values is fairly good. The difference might be attributed *inter alia*

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[1] Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

[2] J. D. Roberts, F. O. Johnson and R. A. Carboni, THIS JOURNAL, **76**, 5692 (1954).

[3] (a) H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952). (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955). (c) H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957); *cf.* also P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

[4] (a) J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953); **76**, 4060 (1954); (b) J. A. Berson, *ibid.*, **76**, 5748 (1954).

[5] J. Weinstock, Abstracts of Papers, American Chemical Society 128th Meeting, Minneapolis, Minn., September 11–16, 1955, p. 19-O.

[6] S. J. Cristol and R. P. Arganbright, THIS JOURNAL, **79**, 603, (1957).

[7] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); E. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[8] H. Kwart and V. A. Rolleri, *Diss. Abstr.*, **19**, 960 (1958).

[9] H. Kwart and L. Kaplan, THIS JOURNAL, **76**, 4072 (1954).

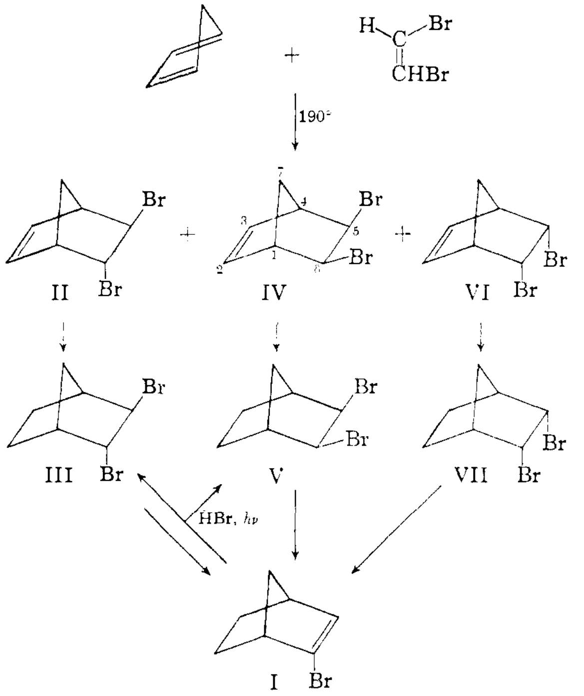
[10] P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955). This value is the apparent carbon–halogen bond moment derived from the measured moments of *cis*-1,2-dihalocyclohexanes. The lowering of 0.2 D. from the value for cyclohexyl bromide was attributed to inductive interaction between the adjacent dipoles.

[11] The dipole moment of norbornylene was found to be the same as that of a normal *cis*-olefin and has a value of 0.40 D. N. L. Allinger and J. Allinger, *J. Org. Chem.*, in press.

[12] W. G. Woods, R. A. Carboni and J. D. Roberts, THIS JOURNAL, **78**, 5653 (1956).

to two factors: (1) repulsion of the bromine atoms resulting in a larger dipole angle and (2) a greater lowering of the individual C–Br moments by the inductive interaction in this rigid molecule. An apparent C–Br moment of 1.70 D., characteristic of the *exo-cis* dihalonorbornyl system, was calculated from the measured moment of V. Employing this value in the calculations, a theoretical moment of 2.84 D. can be derived for IV which differs by only 0.13 D. from the measured μ. The assignment of configuration is unambiguous since it can be seen that hydrogenation of IV to V must be accompanied by an increase in the molecular moment. This was observed experimentally (2.97 → 3.21 D.). Had this product the *endo-cis* configuration (VI) ($\mu_{\text{calcd}} = 3.94$ D.),[13] conversion to its dihydro derivative VII would necessarily result in a lowering of the moment.

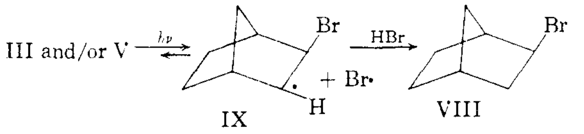
After repeated fractionation of the Diels–Alder reaction mixture, a small amount (<1%) of a third isomer, *endo-cis*-5,6-dibromo-2-norbornene (VI), was recovered. Its structure followed from hydrogenation to *endo-cis*-2,3-dibromonorbornane (VII), which in turn was converted to I. Infrared and gas chromatography analyses showed that V and VII were different isomers and their melting points were depressed on admixture.



The predominant formation of IV instead of the expected VI represents another observation in abeyance with the Alder rules.[14] This example serves to emphasize the risks involved in assigning configurations to the cyclopentadiene adducts with *cis*-1,2-disubstituted ethylenes (and monosubstituted ethylenes) without supporting chemical and physical evidence, particularly in the absence conjugating substituents.

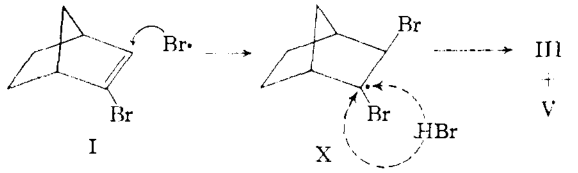
The radical addition of hydrogen bromide to I was effected by irradiating a pentane solution of the vinyl bromide through which gaseous hydrogen bromide was passed at a moderate rate. After workup, the product was distilled so as to avoid fractionation. Infrared and gas chromatography analysis showed that it consisted primarily of a mixture of III and V. These isomers were separated and compared with authentic samples. The results of several runs are summarized in Table I in the Experimental section. From these data, it can be seen that the ratio III/V varies from 2.8 to 1.8 depending on the reaction conditions. Among the byproducts of the reaction, the amounts of which increased with increasing reaction time, were detected two unidentified dibromides and a monobromide component. This monobromide was purified and subsequently identified as *exo*-2-norbornyl bromide (VIII).

Neither III or V was a secondary reaction product resulting from interconversion. This was established by subjecting each pure isomer to *prolonged* reaction conditions. It was found that less than 1% of III was isomerized to V, and a 6% conversion of V to III was observed. Although the major products from these stability studies were the unchanged starting materials, 14–17% of VIII was also detected. This observation coupled with the fact that the monobromide was also formed in the addition reaction leads us to suggest the following mode of formation for VIII. Homolysis of a C–Br bond of either III or V would lead to the intermediate radical IX, which could undergo chain transfer with hydrogen bromide.



The small amount of isomerization of III and V may result from recombination (*i.e.*, free radical bromination) and is supported by the fact that 2% of *endo-cis* isomer VII was formed in the photolysis of III (*i.e.*, the *exo* C–Br bond was homolyzed). In all probability, the unidentified dibromide components that occur in both the addition reaction and the equilibration studies arise *via* bromination of *exo*-2-norbornyl bromide at other positions in the molecule.

Both III and V are the products of non-Markownikoff addition and can be explained by an initial preferred[15] *exo* attack of a bromine atom at the double bond to give X. It is inherent in this process that no *endo-cis*-2,3-dibromonorbornane (VII) can be formed, and we were, in fact, unable to detect the presence of this isomer in the reaction mix-



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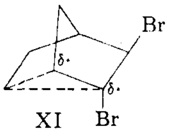
(13) The theoretical dipole moment calculated as for III. In this isomer, the double bond moment strengthens that of the carbon–bromine bonds, the angle being ~40°.

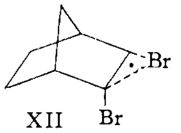
(14) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(15) By analogy with other additions, both ionic and radical, to norbornylene too numerous to mention.

ture. Abstraction of hydrogen atom by X from hydrogen bromide in the chain-carrying step would take place predominantly from the *exo* (*cis* addition) side and also from the *endo*(*trans* addition) side if the process were rapid enough. Therefore, *exo-cis*-2,3-dibromonorbornane (V) represents a *trans* free radical addition to a norbornylene derivative, and its formation in this reaction lends credence to the suggestion that the stereospecificity of hydrogen bromide additions is due to a relatively fast hydrogen abstraction often before conformational changes can take place.[3b,16] Furthermore, a non-classical radical such as XI *cannot* be present. The absence of this type of intermediate in similar reactions has only been inferred, either because of the failure to isolate rearranged products[17] or by the lack of appreciable extra stability of the norbornyl over the cyclohexyl radical.[18] The preponderant formation of III by a *cis* addition process contributes to the overwhelming evidence[16] against the bridged radical XII.



XI



XII

The lack of stereospecificity of the hydrogen bromide addition in this system is indicative of a slow chain-carrying step (relative to the cyclohexyl and acyclic compounds) resulting from various steric repulsions in these bridged structures. The results of runs 1, 2 and 3 in Table I show a slight increase in the ratio of III/V as the concentration of I is increased by a factor of twelve. However, insufficient data are available to note a conclusive trend. Unfortunately, we could not effect the free radical addition in liquid hydrogen bromide since only ionic addition occurred. It is of interest to compare our results with those of Kooyman and Vegter[18] who found that reaction of the norbornyl radical with chlorine and bromine formed 70% *exo* product.

In conclusion, it should be mentioned that the products III and V, the result of the "abnormal" addition, are without doubt formed by a radical process. The ionic addition of hydrogen bromide leads to isomeric dibromides.[19,20]

Acknowledgment.—The author is indebted to the Graduate School, Wayne State University, for a Graduate Faculty Research Fellowship, and to Mr. James C. Powers for technical assistance.

Experimental[21]

Diels–Alder Addition of Dibromoethylene to Cyclopentadiene.—Typical reaction conditions for formation of the adduct employed 127 g. (1.92 moles) of freshly prepared cyclopentadiene and 460 g. (2.47 moles) of 1,2-dibromoethylene (Eastman or MCB, b.p. 107–110°; consisting of 61% *trans*, 39% *cis* isomer as shown by gas chromatography). These materials were placed in a stainless steel reaction vessel under 350 p.s.i.g. nitrogen pressure and heated to 180–190° for 4–6 hours. The dark colored product was distilled from a Claisen flask to give 110 g. of forerun (mainly recovered dibromoethylene), 254 g. of distillate, b.p. 40–90° (1 mm.), which contained 28.6 g. of crystalline material. This solid was separated and washed with pentane; and the mother liquors and washings were redistilled though a 0.7 × 61 cm. tantalum spiral column. There was obtained 120 g. of liquid dibromide fractions (24%), b.p. 59.5–70° (0.8 mm.), n^{25}_{D} 1.5652–1.5672, and an additional 10 g. of solid.

The combined crystalline product was fractionally crystallized from ether. All crops had the same melting points and showed no depression on admixture. The total yield of *exo-cis*-5,6-dibromo-2-norbornene (IV), m.p. 116.5–117.5° after crystallization from ethyl acetate, was 38.6 g. (8%).

Anal. Calcd. for $C_7H_8Br_2$: C, 33.36; H, 3.20; Br, 63.43. Found: C, 33.52; H, 3.25; Br, 63.47.

Careful fractionation of the liquid dibromide mixture furnished 70.4 g. of *trans*-5,6-dibromo-2-norbornene (II), b.p. 47–48° (0.3 mm.) (57–58° at 0.8 mm.), n^{25}_{D} 1.5665.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.36; H, 3.20; Br, 63.43. Found: C, 33.52; H, 3.20; Br, 63.74.

Gas chromatography of this isomer through a column containing 30% by weight Silicone 550 fluid on 30–80 mesh firebrick at 180° indicated 98–100% purity.

A higher boiling isomer, b.p. 67–70° (0.8 mm.), n^{25}_{D} 1.5719, was also obtained and was assigned the *endo-cis* structure VI. The retention time in gas chromatography of VI was different from those of the *trans* (II) and *exo-cis* (IV) isomers.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.36; H, 3.20; Br, 63.43. Found: C, 33.59; H, 3.29; Br, 63.49.

The Diels–Alder reaction was also carried out in a Pyrex tube which had been flushed with nitrogen before sealing, and then was heated at 190° for 4 hours. From 27.6 g. (0.42 mole) of cyclopentadiene and 100 g. of dibromoethylene there was obtained 2.3 g. of *exo-cis*-dibromide IV and 15.41 g. of liquid dibromides. Careful fractionation of this material gave the following fractions:

Fraction	B.p.		n^{25}_{D}	Wt., g.	Composition,[a] %	
	°C.	Mm.			II	VI
1	To 44	0.3	....	...		
2	44–45	.3	1.5657	8.1	86	14
3	45–49	.3	1.5660			
4	45–49.5	.35	1.5655	0.54		
5	50–55	.35	1.5650	0.63	75	24
6	55–60	.35	1.5678	3.5	19	69.7[b]
				12.77		

[a] Determined by gas chromatographic analysis through a column containing 30% by weight Silicone 550 fluid on firebrick at 178°. [b] Contains 11.3% of an unidentified product with a retention time slightly greater than that of VI.

trans-**2,3-Dibromonorbornane (III).**—A solution of 103 g. (0.4 mole) of II in 125 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure in the presence of 2.0 g. of prereduced platinum oxide. After 115 minutes, 106% of the theoretical quantity of hydrogen was consumed. The catalyst was filtered and the solvent was removed by distillation. Distillation of the residue afforded 97 g. (93%) of *trans*-2,3-dibromonorbornane (III), b.p. 63–64° (0.4 mm.), n^{25}_{D} 1.5560 (lit.[9] b.p. 62–63° at 0.4 mm., n^{20}_{D} 1.5618).

exo-cis-**2,3-Dibromonorbornane (V).**—Hydrogenation of 25 g. (0.099 mole) of IV was carried out in ethyl acetate in the manner described for the *trans* isomer. The catalyst was filtered and the filtrate was evaporated to dryness to yield a crystalline solid. Recrystallization from absolute methanol furnished 23 g. (91%) of *exo-cis*-2,3-dibromonorbornane (V), m.p. 60.4–61.3°. The infrared spectrum of V (Nujol mull) is characterized by the following bands which are absent in the spectra of III and VII: 742(s),

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[16] P. S. Skell, R. C. Woodworth and J. H. McNamara, THIS JOURNAL, **79**, 1253 (1957).

[17] See S. J. Cristol, G. D. Brindell and J. A. Reeder, *ibid.*, **80**, 635 (1958), and references cited therein.

[18] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); see also S. J. Cristol and G. D. Brindell, THIS JOURNAL, **76**, 5699 (1954).

[19] N. A. LeBel and J. C. Powers, to be published.

[20] We have been informed that Dr. H. Kwart and Mr. J. Nyce have also carried out investigations similar to ours. We are exchanging manuscripts.

[21] Melting points are corrected and boiling points are uncorrected. Infrared spectra were carried out on a Beckman IR-4 recording spectrophotometer with sodium chloride optics.

945(s), 950(s), 970(m), 1177(m), 1215(s), 1255(s) and 1330(s) cm.$^{-1}$.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97; Br, 62.93. Found: C, 32.89; H, 3.94; Br, 62.77.

endo-cis-**2,3-Dibromonorbornane (VII).**—Hydrogenation of 5.4 g. (0.02 mole) of VI afforded a product which crystallized on attempted distillation. Recrystallization from absolute methanol gave VII, m.p. 55.3–55.6°. The melting point was depressed below 25° on admixture with V. The infrared spectrum (Nujol mull) shows bands at 735(w), 760(m), 793(m), 806(s), 936(m), 945(s), 1035(w) and 1147(m) cm.$^{-1}$.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97; Br, 62.93. Found: C, 33.05; H, 4.14; Br, 62.75.

Under typical conditions the retention times for the three isomers in gas chromatography on a 6′ × 8 mm. Silicone 550 column (30% by weight on 30-80 mesh firebrick) at 187° were: *trans* (III), 22 minutes; *endo-cis* (VII), 37 minutes; *exo-cis* (V), 41 minutes.

2-Bromo-2-norbornene (I). A. From *trans*-**2,3-Dibromonorbornane (III).**—A modification of the procedure of Kwart and Kaplan[9] for the dehydrobromination was followed employing 95 g. (0.37 mole) of III in 50 ml. of *t*-butyl alcohol and a boiling solution of 14.9 g. (0.38 mole) of potassium in 250 ml. of *t*-butyl alcohol. The dried ether extract was distilled and the residue was saved. To the distillate was added 300 ml. of pentane and this solution was extracted with five 1-l. portions of water. The pentane layer was dried and concentrated. The residue was combined with that obtained earlier and distilled to give 48 g. (74%) of the vinyl bromide, b.p. 57–58° (16 mm.), n^{25}D 1.5177 (lit.[9] b.p. 61–63° at 16 mm., n^{20}D 1.5058). The infrared spectrum of I was similar to that reported.[9]

Anal. Calcd. for C_7H_9Br: C, 48.58; H, 5.24; Br, 46.18. Found: C, 48.38; H, 4.81; Br, 46.25.

B. **From** *exo-cis*-**2,3-Dibromonorbornane (V).**—Twenty grams (0.079 mole) of V was treated with potassium *t*-butoxide (from 3.13 g. of potassium in 75 ml. of boiling *t*-butyl alcohol). It was necessary to add the solid dibromide in portions. After 16 hours, 100 ml. of water was added and the aqueous solution was extracted with two 150-ml. portions of pentane. The combined pentane solutions were extracted with three 500-ml. portions of water, dried and concentrated. The residue on distillation afforded 11.3 g. (83%) of product, b.p. 57–58° (16 mm.), n^{25}D 1.5177. The infrared spectrum of the olefinic bromide was identical with that of 2-bromo-2-norbornene (I), as were the retention times in gas chromatography.

C. **From** *endo-cis*-**2,3-Dibromonorbornane (VII).**—Dehydrobromination of 1.5 g. of VII also produced 2-bromo-2-norbornene (I), identified by its infrared spectrum and by gas chromatography.

Radical Addition of Hydrogen Bromide to 2-Bromo-2-norbornene.—A solution of 3.0 g. (0.017 mole) of 2-bromo-2-norbornene in 200 ml. (1.7 moles) of purified pentane was placed in a reaction flask and cooled to 0°, after which nitrogen was passed through for 15 minutes. The solution was irradiated with a Hanau S-81 quartz immersion lamp during which time gaseous hydrogen bromide (dry) was bubbled through at a gentle rate. The reaction was allowed to proceed for 15 minutes. The excess hydrogen bromide was removed by washing with 20 ml. of water, followed by three 20-ml. portions of 10% sodium carbonate solution and finally 20 ml. of water. After being dried over anhydrous potassium carbonate, the pentane was removed and the residue, distilled so as to avoid fractionation, furnished 3.91 g. (89%) of product, b.p. 61–73° (0.7 mm.), n^{25}D 1.5178.

Examination of the infrared spectrum of this product indicated a mixture consisting mainly of *trans*- and *exo-cis*-2,3-dibromonorbornane (III and V, resp.). Analysis by gas chromatography through the Silicone oil column showed the composition given under run 1 in Table I.

Careful fractionation of the mixture afforded III in the first fractions as shown by the infrared spectrum and gas chromatography; whereas crystalline *exo-cis* material separated from the last fraction. Recrystallization from methanol gave pure V, m.p. and m.m.p. 58.5–60°. The mixture melting point with VI was depressed.

The mixtures resulting from several addition reactions were combined and distilled, and the volatile (monobromide) component was separated. Redistillation gave a product, n^{25}D 1.5129, which had an identical infrared spectrum with that of *exo*-2-norbornyl bromide (VIII) (lit.[22] b.p. 82 at 19 mm., n^{25}D 1.5126). Gas chromatography on a column containing 30% by weight of *tris*-2-cyanoethoxypropane on Chromosorb supported this assignment.

TABLE I

No.	Concn., g. of I/100 ml. pentane	Temp., °C.	Time, min.	Yield, %	III/V	III, %	V, %	VIII, %	Other dibromides
1	1.5	0	15	89	2.5	65	26	4	5
2	0.25	0	15	97	2.4	59	25	12	4
3	3.0	0	15	91[a]	2.8	68	24	3	6
4	1.2	0	120	70	2.4	55	23	7	15
5	1.5	−25	15	89	2.1	62	30	5	3
6	1.33	−25	60	79	2.5	62	25	5	8
7	1.5	−65	15	88	1.8	61	35	2	3
8	1.0	−65	25	85	2.2	62	28	2	8
9	1.0	−65	120	90	1.9	48	27	5	20

[a] Based on recovered vinyl bromide.

The data in Table I are the results of several reactions in which the concentration of I, time and temperature (−25°, Dry Ice–carbon tetrachloride; −65°, Dry Ice–acetone) were varied.

Stability Studies. Irradiation of III and V in the Presence of Hydrogen Bromide.—A solution of 3 g. of *trans*-2,3-dibromonorbornane (III) in 250 ml. of purified pentane was irradiated at −25° (Dry Ice–carbon tetrachloride) for 2 hours while dry hydrogen bromide was bubbled in. After removal of the excess hydrogen bromide in the usual manner, the pentane solution was dried and concentrated and the residue was distilled to give 2.33 g. (78%), b.p. 71° (1 mm.), n^{25}D 1.5507. Gas chromatography analysis of the mixture showed that the major product (75%) was recovered III. Less than 1% of V was detected. Other products included 13% of exo-2-norbornyl bromide (VIII), 3% of unidentified monobromides, 7% of other dibromides and 2% of *endo-cis* isomer VI.

A similar reaction was carried out on 2 g. of *exo-cis*-2,3-dibromonorbornane (V) in 250 ml. of pentane. After workup, distillation of the pentane afforded 1.46 g. (75%) of residue which was analyzed and found to consist of: 73% recovered V, 6% of III, 17% of VIII, and 2% each of unidentified mono- and dibromides.

Dipole Moments.—The apparatus used for the dielectric constant measurements has already been described.[23] Reagent grade benzene, distilled just before use, was the sol-

TABLE II

DIELECTRIC CONSTANTS OF *exo-cis*-5,6-DIBROMO-2-NORBORNENE (IV)

N_2	ϵ	d	
0.0041760	2.3223	0.8788637	α 12.6645; $\epsilon_{1,2}$ 2.2689
.0020956	2.2961	.8756806	
.0011541	2.2800	.8742188	β 1.52185; d_1 0.8724705
.0005342	2.2769	.8732206	
.0000000	2.2702	.8724824	$P_{2\infty}$ 226.0695 cc.; M_D 45.189 cc.
			μ 2.97 ± 0.02 D.

DIELECTRIC CONSTANTS OF *exo-cis*-2,3-DIBROMONORBORNANE (V)

N_2	ϵ	d	
0.0030717	2.3116	0.8771380	α 14.6121; $\epsilon_{1,2}$ 2.2668
.0027221	2.3066	.8765882	
.0022032	2.2994	.8757544	β 1.52252; d_1 0.8724134
.0014475	2.2879	.8745683	
.0007858	2.2780	.8735944	$P_{2\infty}$ 255.6213 cc.; M_D
.0000000	2.2670	.8724127	45.656 cc.
			μ 3.21 ± 0.02 D.

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[22] J. D. Roberts, E. R. Trumbull, J. W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[23] M. T. Rogers, *ibid.*, **77**, 3681 (1955). We are indebted to Dr. N. L. Allinger and Dr. J. Allinger for these measurements and to Dr. M. T. Rogers whose instrument was used.

vent. The dielectric constants and densities of solutions of various mole fractions were measured at 25° and are listed in Table II. Calculations of the molar polarization were carried out by the method described earlier.[24] The molar refractivities were obtained by addition of the atomic refractivities[25] and the dipole moments were calculated by use of the Debye equation.

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[24] L. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942); see also N. L. Allinger, *ibid.*, **79**, 3443 (1957).

[25] J. A. Leermakers and A. Weissberger in H. Gilman's "Organic Chemistry," Vol. II, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.

DETROIT, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

The Synthesis of 2,7-Disubstituted Norbornanes

BY C. H. DEPUY AND P. R. STORY[1]

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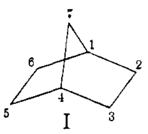
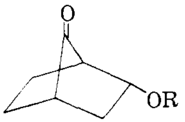
A general method for the preparation of 7-keto-norbornanes substituted in the 2-position is reported. The reaction sequence involves the addition of α-acetoxyacrylonitrile to dimethylfulvene, hydrolysis to the ketone, reduction of the carbonyl group and the endocyclic double bond, and ozonolysis. The stereochemistry of lithium aluminum hydride and lithium tri-*t*-butoxyalumino hydride reduction in this and similar systems was investigated and some observations are made about the effect of substituents on the selectivity of catalytic hydrogenation. The keto-acetate IIb is extremely sensitive to base, and hydrolysis is accompanied by ring opening.

The norbornane system I has been one of the most fruitful of all arrangements of atoms for the study of reaction mechanisms. Derivatives of this system exhibit some of the best examples of anchimeric assistance, transannular interactions and steric inhibition to solvolysis to be found in the chemical literature. Indeed, most of the common principles of organic reaction mechanisms could be well illustrated by the reactions of variously substituted norbornanes. Only three structurally isomeric monosubstituted norbornanes can exist.



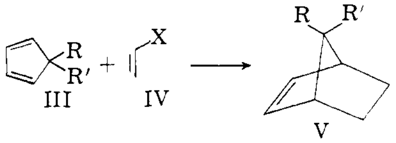
I



II

A number of excellent methods[2,3] are available for the synthesis of the stereoisomeric 2-substituted compounds and for the so-called bridgehead or 1-substituted norbornanes. Very few 7-substituted compounds have been prepared, however, and the reported methods did not seem very attractive for the studies in which we were interested. We were, consequently, led to the development of a new, general synthesis of 7-ketonorbornanes which allowed, at the same time, the introduction of substituents of known stereochemistry at the 2-position (II). It was anticipated that the precisely known geometry[4] of this bicyclic system would allow a careful study of transannular interactions in nucleophilic reactions to be made, and it was planned also to investigate the properties and reactivity of carbonyl groups in this unique position. The results of some of these studies will be published soon, but it was thought that the synthesis of these molecules was of sufficient interest, and enough potential utility, to warrant separate publication.

At first sight, substituents could easily be introduced at the seven position by a Diels-Alder reaction of a suitably substituted cyclopentadiene (eq. 1). In practice, however, compounds of type III are not at all available. The most favorable compound, cyclopentadienone (III, R,R′ = O), is unknown, and monosubstituted cyclopentadienes (*e.g.*, III, R = H, R = OAc) tautomerize readily due to the acidic proton on the cyclopentadiene ring.[5] 7-Substituted norbornanes have been prepared by rearrangement reactions of bicycloheptadiene and derivatives[6,7] and from acetoxycyclopentadiene and ethylene.[8]



(1)

We determined to attempt the synthesis of II by making use of the Diels-Alder reaction of equation 1 with one of the few types of readily available substituted cyclopentadienes, the fulvenes (III, R,R′ = CR_2). These compounds were known to be reactive in the Diels-Alder reaction,[9] and the product, which would contain a double bond at the 7-position, could be further elaborated through this center of unsaturation. Alder and Ruhmann,[10] and Kohler and Kable[11] had treated a double bond of this type with ozone, and more recently Wilder and Winston[12] had isolated a 7-ketone by this method. There remained the problem of a suitable choice for the dienophile IV. Fortunately, an excellent dienophile for our purpose, α-acetoxyacrylonitrile (VII), has recently been introduced by Bartlett and Tate.[13] This dienophile has the advantage of re-

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[1] Union Carbide Fellow, 1958–1959.

[2] J. D. Roberts, C. C. Lee and W. H. Saunders, THIS JOURNAL, **76**, 4501 (1954).

[3] Elsevier's "Encyclopedia of Organic Chemistry," Vol. 12A, Elsevier Publishing Co., Inc., New York, N. Y., 1948, p. 628.

[4] H. Krieger, *Suomen Kem.*, **31B**, 348 (1958).

[5] M. Rosenblum, THIS JOURNAL, **79**, 3179 (1957).

[6] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[7] S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

[8] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[9] J. H. Day, *Chem. Revs.*, **53**, 167 (1953).

[10] K. Alder and R. Ruhmann, *Ann.*, **566**, 1 (1950).

[11] E. P. Kohler and J. Kable, THIS JOURNAL, **57**, 917 (1935).

[12] P. Wilder and A. Winston, *ibid.*, **78**, 868 (1956).

[13] P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956).