40 ml of a 3 *M* solution of diborane in THF. After 1 additional hr at room temperature and oxidation with hydrogen peroxide the solution was extracted with ether and distilled yielding 5 g of a product, bp 80–82° (25 mm), $\bar{\nu}_{max}$ (neat) 3330 cm^{-1}.

Anal. Calcd for $C_7H_{14}O$: C, 73.7; H, 12.3. Found: C, 73.7; H, 12.3.

This mixture of isomers could not be separated by glpc on a series of columns. Finally, the analysis was performed by two determinations. A 17-ft column of 10% Diglycerol on acid-washed Chromosorb P separated a mixture of XXVI and XXVII from XXV and XXVIII (ratio 47:53). These two latter alcohols were separated only partially. The mixture of alcohols was therefore oxidized and the mixture of ketones was analyzed on the same column. The percentages of all the alcohols were obtained by a combination of the two determinations.

Oxidation of the Product of Hydroboration of XXIV.—A solution of 1 g of chromic acid and 1.6 g of sulfuric acid in 4 ml of water was added dropwise during 10 min to a solution of 4 g of the mixture of alcohols in 40 ml of acetone cooled to $-5°$; the reaction mixture was left for 1 hr at 0°. Several drops of methanol were then added to decompose excess of chromic acid. The solution was filtered and the precipitate was washed with methanol. The filtrate was concentrated *in vacuo*, water (50 ml) was added, and the product was extracted five times with 30-ml portions of dichloromethane. Evaporation of the solvent left 3.2 g of a residue, that was analyzed by glpc, showing that 60% of the alcohols were oxidized to ketones and that the ratio of peaks of the remaining alcohols changed only slightly relative to the starting material. The axial alcohols were oxidized somewhat more rapidly and the ratio of (XXVI + XXVII)/(XXV + XXVIII) was now 42:58. 3-Methylcyclohexanone (Aldrich), 4-methylcyclohexanone (Fluka), and 4-methylcyclohexene (Aldrich) of reference were commercial products. The alcohols of reference were obtained by reduction of the ketones with lithium aluminum hydride, which gave mixtures of known proportion of isomers.[27]

Registry No.—I, 6493-77-2; II, 4841-84-3; III, 7731-15-9; VIII, 7731-16-0; IX, 7775-57-7; X, 7771-14-4; XIII, 7731-17-1; XIV, 7731-18-2; XVI, 7731-19-3; XVIII, 933-12-0; XIX, 2518-25-4; XX, 933-48-2; XXI, 767-54-4; XXII, 7731-23-9; XXIII, 503-46-8; XXV, 5454-79-5; XXVI, 7443-55-2; XXVII, 7731-28-4; XXVIII, 7731-29-5.

Acknowledgment.—We are grateful to Dr. M. Rabinowitz for the determination of the nmr spectrum of XVIII.

[27] E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.* **79**, 5992 (1957).

Directive Effect of the Cyclopropyl Group in Hydroboration

Shinya Nishida, Ichiro Moritani, Kazuomi Ito, and Kiyoki Sakai

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka, Japan

Received September 13, 1966

Vinylcyclopropane and spiro[2.5]oct-4-ene are hydroborated by diborane in dry tetrahydrofuran; the organoboranes formed are oxidized by alkaline hydrogen peroxide. An analysis of the resulting carbinol mixtures has revealed that vinylcyclopropane produces cyclopropylmethylcarbinol and 2-cyclopropylethanol in the ratio 3:97, while spiro[2.5]oct-4-ene gives a mixture of spiro[2,5]octan-4-ol and -5-ol in the ratio 22:78. Compared with the ratio of isomeric carbinols observed in ordinary terminal and internal olefins, these two olefins under consideration exhibit different product distributions, *i.e.*, a marked increase in β alcohol is to be noted. From this it may be safely assumed that the cyclopropyl group is more electron releasing than other alkyl groups.

A number of extensive studies in the directive effect of various substituents in hydroboration[1] have made it clear that the electronic effect of the substituent is one of the important factors controlling the direction of boron attack where diborane is utilized. With cyclopropyl, however, no comparable work is available as yet, but its unique double-bond character[2-4] ought to lead to significant observations and fruitful discussions about the possible behavior of cyclopropyl group in hydroboration, *e.g.*, whether it works as an alkyl group or as an unsaturated group in its influence on the direction of boron attack. The present paper aims to discuss the directive effect of cyclopropyl group from this point of view with reference to both terminal and internal olefins.

Results

Olefins investigated were vinylcyclopropane (**1**), vinylcyclohexane (**2**), and spiro[2.5]oct-4-ene (**3**). Olefin **1** was obtained by the reductive debromination[5] of 2,2-dibromo-1-vinylcyclopropane, prepared by the addition of dibromocarbene to 1,3-butadiene;[6] olefin **2** was a commercial product; olefin **3** was obtained by the thermal decomposition of spiro[2.5]oct-4-yl xanthate, the purities of these olefins being 97–98.5% on vpc analysis. The external hydroboration technique[7] was employed. The organoboranes formed were oxidized by alkaline hydrogen peroxide,[7] and the resulting alcohol mixtures were subjected to vpc analysis. The results are shown in Table I.

The major product in each case was isolated and characterized as indicated below. 2-Cyclopropylethanol was converted to crystalline phenylurethan, mp 63.9–64.1°, and β-naphthalenesulfonate, mp 26.0–27.0°. The analytical results and nmr and infrared spectra were in accordance with the 2-cyclopropylethyl structure. 2-Cyclohexylethanol was derived to the known 3,5-dinitrobenzoate, mp 71.3–71.8° (lit.[8] mp 71–72°). The structure of spiro[2.5]octan-5-ol was established by the comparison with authentic material, prepared from 3-methylenecyclohexanol *via* the Simmons–Smith reaction.[9] A mixture melting point of the 3,5-dinitrobenzoate, mp 98.4–99.4°, from both samples, showed no depression. The minor component was checked against authentic material by comparing its retention time on vpc.

In runs 1, 2, and 3, 2-cyclopropylethanol was isolated in 71–82% yield, while a mixture of spiro[2.5]-

---

[1] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[2] M. Y. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).

[3] M. Charton, *J. Chem. Soc.*, 1205 (1964), and references cited therein.

[4] A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964), and references cited therein.

[5] W. E. von Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

[6] R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

[7] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[8] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

[9] I. Moritani and T. Tsuji, the manuscript in preparation.

TABLE I

PRODUCT DISTRIBUTIONS IN THE HYDROBORATION–OXIDATION OF VINYLCYCLOPROPANE (1), VINYLCYCLOHEXANE (2), AND SPIRO[2.5]OCT-4-ENE (3)

Run	Olefin	Temp,[a] °C	Mole ratio of olefin/ BH_3	Carbinol[b] % α attack	Carbinol[b] % β attack
1	1	−10	1:1	3[c]	97[d]
2	1	−10	1:$^1/_3$	3[c]	97[d]
3	1	−30	1:1	3[c]	97[d]
4	1	−30	1:$^1/_3$	4[c]	96[d]
5	2	0	1:1	6[e]	94[f]
6	2	20	1:$^1/_3$	8[e]	92[f]
7	3	0	1:1	21[g]	79[h]
8	3	0	1:$^1/_3$	24[g]	76[h]
9	3	−60	1:$^4/_3$	22[g]	78[h]

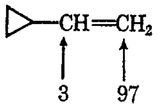
[a] A temperature of the hydroborating flask. [b] In runs 1–4, two other very minor peaks (<2%) were detected, which were neither cyclopentanol nor cyclobutylcarbinol. In runs 7–9, a broad, unidentified peak, corresponding to approximately 12% of total area, appeared after a far longer retention. The figures given are normalized. [c] Cyclopropylmethylcarbinol. [d] 2-Cyclopropylethanol. [e] Cyclohexylmethylcarbinol. [f] 2-Cyclohexylethanol. [g] Spiro[2.5]octan-4-ol. [h] Spiro[2.5]octan-5-ol.

octan-4-ol and -5-ol was isolated in 81.5% yield in run 7.

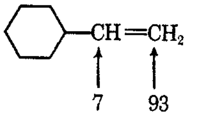
Discussion

The present experiment has clearly shown that reaction products virtually retain the cyclopropane structure, which may be taken to imply that the cyclopropane ring conjugated with a double bond does not suffer any appreciable cleavage under hydroboration–oxidation procedure. Recently Rickborn and Wood[10] have reported a cleavage of cyclopropanes with diborane, indeed, but the cleavage in that case had resulted in the absence of an ethereal solvent at a relatively high temperature (100°). That is certainly irrelevant here and it is to be concluded, therefore, that cyclopropane rings will generally survive the hydroboration conditions.[1,7]

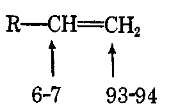
As is shown in Table I, the directive effect of the cyclopropyl group in hydroboration deserves our attention. In the case of monosubstituted terminal olefins, previous investigations[1] have established that boron atom is placed predominantly at the terminal position in 93–94% (**4**, **5**, and **6**). It is to be noted that vinylcyclohexane (**2**) exhibits the same product distribution. However, vinylcyclopropane (**1**) is seen to undergo hydroboration with a greater preference for terminal attack (97%) than that observed in **2**, **4**, **5**, and **6**. This interesting effect is more manifest in the internal olefin. It is well known that, in the hydroboration of disubstituted internal olefins, boron becomes attached almost equally to each one of the two olefinic carbons.[1] As a typical example, 3,3-dimethylcyclohexene (**7**) gives a mixture of 50% α and 50% β alcohol.[1] However, in spiro[2.5]oct-4-ene (**3**), more boron comes to the β position (78%). Apparently, a cyclopropyl group exerts an interesting effect on the direction of boron attack such that it places a greater amount of boron at the position β to the cyclopropyl group.



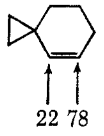
1



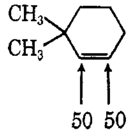
2



4, R = ethyl
5, R = isopropyl
6, R = *t*-butyl

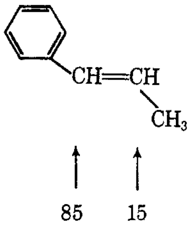


3

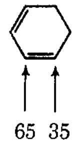


7

In view of the fact that the steric hindrance cannot be an important factor controlling the direction of boron attack when diborane is utilized,[1] the product distribution observed in the present study should be attributed to the electronic effect of the cyclopropyl group. According to its double-bond character,[2–4] the cyclopropyl group might exhibit an effect similar to that of an unsaturated group, such as vinyl or phenyl. Indeed, it is known that cyclopropanecarboxylic acid is weakly more acidic,[11–13] as is benzoic acid,[11] than other cycloalkanecarboxylic acids. However, this is not the case in hydroboration, and an interesting contrast comes out when the present result is compared with the direction taken in styrene derivatives.[1] *trans*-2-Methylstyrene (**8**) is known to be hydroborated preferentially at the α position, whereas olefin **3** reacts preferentially at β. Compared to an alkyl group, the directive effect of the cyclopropyl group is thus in the opposite direction to that of phenyl. A similar directive influence of vinyl group is seen in the monohydroboration of cyclohexa-1,3-diene (**9**) by diborane; boron makes its attack predominantly at the position α to the other double bond.[14]



8



9

In the hypothesis of the polarized transition state suggested by Brown,[1] one of the important factors controlling the anti-Markovnikov addition of boron to ordinary alkene is said to be an electron-releasing effect of the alkyl group.[1] In styrene derivatives, it is suggested that the phenyl group can not only stabilize the transition state **10** by supplying electron density; it can also stabilize transition state **11** by absorbing electron density.[1] Consequently, the attack of boron atom at the α position of olefin is more enhanced than that observed in alkenes. After these discussions, the present results would seem to be fairly significant. It is clear that the cyclopropyl group differs greatly

---

[10] B. Rickborn and S. E. Wood, *Chem. Ind.* (London), 162 (1966).

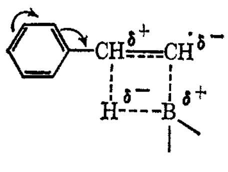
[11] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962, p 124.

[12] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

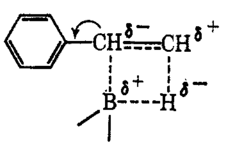
[13] M. Kilpatrick and J. G. Morse, *ibid.*, **75**, 1854 (1953).

[14] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

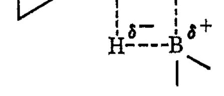
from unsaturated group, such as phenyl, and it stabilizes particularly transition state **12** by supplying electron density. Moreover, the degree of electron supply here exceeds that of alkyl groups. A special feature of a cyclopropyl group consists in that it interacts electronically with an adjacent olefinic group only in such a manner that it supplies an electron, and this is also observed in the ultraviolet study of *para*-substituted phenylcyclopropanes.[15]



10



11



12

An electron-donating character of cyclopropyl group to an adjacent electron-deficient center is most strikingly demonstrated in cyclopropylcarbinyl cation,[16-19] and recent investigations have shown that the maximum interaction can be achieved with the bisected conformation.[20-23] Similarly, the bisected conformation is also important for the interaction of cyclopropane with an adjacent olefinic group.[24,25] In the present case, olefin **3** is structurally fixed in a bisected conformation so that the electronic interaction has overcome the electron-withdrawing inductive effect of the cyclopropyl group.[12] Vinylcyclopropane (**1**) is also capable of taking a bisected conformation.

Finally, it will be of interest to point out[26] that the relative effects of the three groups in directing hydroboration, cyclopropyl > methyl > phenyl, are reflected in the relative values of σ_p^+, −0.484,[23] −0.311,[27] and −0.179,[27] respectively.

Experimental Section[28]

Vinylcyclopropane (**1**).—2,2-Dibromovinylcyclopropane, bp 60–66° (20 mm), was obtained in 67% yield by the addition of dibromocarbene to 1,3-butadiene.[6] The infrared spectrum was superimposable with that reported in the literature.[6] Since this dibromo compound was rather sensitive to light and oxygen in the air, it was debrominated[5] without further purification.

A 3-l., four-necked flask was equipped with a mechanical stirrer, a pressure-equalized dropping funnel, and an air condenser, the top of which was led to a Dry Ice cooling trap through a long, spiral condenser. In this flask, 129 g (0.571 mole) of 2,2-dibromovinylcyclopropane and 300 ml of dioxane were introduced. The fourth neck was stoppered and the solution was cooled with running water. While a mixture of 1500 ml of ethanol (95%) and 50 ml of distilled water was added dropwise from the dropping funnel, small pieces of metallic sodium, total of 212 g (9.22 g-atom), were added intermittently from the fourth neck. After the addition of metallic sodium was completed and the reaction ceased, 900 ml of water was added to the reaction mixture and the flask was heated on a water bath at 60–70° for 1 additional hr. The reaction product collected in the Dry Ice trap was dried by metallic sodium and distilled through a 45-cm Widmer distilling column. A fraction boiled at 37.0–40.0° (22.6 g, 58% yield) was collected and it was rectified by means of a 60-cm Helipack fractionating column. There was obtained vinylcyclopropane (95% pure on vpc): bp 40.0–40.2°, $n^{20}\mathrm{D}$ 1.4137 (lit.[29] bp 40.19°, $n^{20}\mathrm{D}$ 1.4138). The infrared spectrum was superimposable with reported one.[29] A further purification by preparative vpc gave vinylcyclopropane of 96–97% purity, which was used for the further investigation.

Spiro[2.5]oct-4-yl Xanthate.—The sodium borohydride reduction of 2-N,N-dimethylaminomethylcyclohexanone[30] afforded the corresponding cyclohexanol in 48% yield. A thermal decomposition of its N-oxide[31] gave 2-methylenecyclohexanol[32] in 45% yield. An application of the Simmons–Smith reaction to 2-methylenecyclohexanol gave spiro[2.5]octan-4-ol: bp 65–67° (7 mm), $n^{25}\mathrm{D}$ 1.4781 [lit.[33] bp 76–78° (20 mm), $n^{25}\mathrm{D}$ 1.4772], 72% yield. 3,5-Dinitrobenzoate melted at 113.2–114.2° and showed a satisfactory elemental analysis.[9]

Spiro[2.5]oct-4-yl xanthate was prepared by the reaction of sodium spiro[2.5]octan-4-oxide with carbon disulfide and methyl iodide in dry ether.[34] Solid precipitates were removed by a filtration and the solvent was removed under the reduced pressure. Recrystallizations of the solidified residue from low-boiling petroleum ether gave white, crystalline xanthate, mp 30.5–31.5°, in 58.4% yield.

Anal. Calcd for $C_{10}H_{16}OS_2$: C, 55.51; H, 7.45. Found: C, 55.61; H, 7.55.

Spiro[2.5]oct-4-ene (**3**).—Spiro[2.5]oct-4-yl xanthate was decomposed at 120–200° in 2 hr according to the procedure described by Alexander and Mudrak.[34] A fractional distillation of the reaction product collected in a Dry Ice cooling trap gave olefin boiling at 129–130°, $n^{25}\mathrm{D}$ 1.4740, in 62% yield (98.5% pure on vpc).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.50; H, 11.20.

This olefin exhibited characteristic infrared absorptions at 3000 and 1010 for a cyclopropane, and at 3065 and 1640 cm^{-1} for a double bond. Signals observed in the nmr spectrum were a singlet at τ 9.54 (four hydrogens), a multiplet at 8.60–7.85 (six hydrogens), a doublet at 5.05 (one hydrogen, J = 10 cps), and a multiplet at 4.30–4.55 (one hydrogen). These spectral results confirmed the structure of spiro[2.5]oct-4-ene.

Hydroboration–Oxidation and the Analytical Procedure.—An external hydroboration technique[7] was employed; a desired quantity of diborane was generated and bubbled through a solution of olefin (75 mmoles) in 30 ml of dry tetrahydrofuran. The solution was cooled by a suitable cooling mixture during

---

(15) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964).

(16) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

(17) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

(18) (a) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959); (b) H. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962).

(19) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

(20) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965).

(21) (a) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965); (b) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

(22) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).

(23) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

(24) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

(25) (a) W. Lüttke and A. de Meijere, *Angew. Chem.*, **78**, 544 (1966); (b) W. Lüttke, A. de Meijere, H. Wolff, H. Ludwig, and H. W. Schrötter, *ibid.*, **78**, 141 (1966).

(26) The authors are indebted to Professor H. C. Brown of Purdue University, Lafayette, Ind., who has kindly suggested this point.

(27) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(28) Melting points were determined by a liquid bath and are corrected; boiling points are uncorrected. Infrared spectra were recorded by a Hitachi EPI-S2 infrared spectrophotometer; ultraviolet spectra were obtained by a Hitachi EPS-2U spectrophotometer. Nmr spectra were recorded either by a Varian A-60 spectrometer or by a Japan Electron Optics JNM-4H-100 spectrometer. Vpc analyses were made by a Yanagimoto GCG-3 gas chromatograph. Microanalyses were done by the Microanalytical Laboratory, Faculty of Engineering and Faculty of Engineering Science, Osaka University, Osaka, Japan.

(29) V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4930 (1952).

(30) (a) C. Mannich, *Arch. Pharm.*, **265**, 251 (1927); (b) C. Mannich and R. Braun, *Chem. Ber.*, **53**, 1874 (1920).

(31) A. C. Cope and E. Ciganek in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 612.

(32) A. S. Drieding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

(33) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(34) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

the reaction (see column 3 in Table I). Resulting organoboranes were oxidized by alkaline hydrogen peroxide,[7] and the carbinol mixture was extracted with three portions of ether. The combined ether solution was dried over anhydrous magnesium sulfate, and the concentrated ether solution was injected into vpc for quantitative analysis. The reaction conditions and the results of analyses are given in Table I.

A major component in the product was isolated and its structure was established as described later. A minor component was ascertained by comparing its retention time on vpc with that of authentic material. In the case of vinylcyclopropane (**1**), analyses were made under the following vpc conditions: (i) glycerol at 75°, (ii) silicone DC-550 at 90°, and (iii) Carbowax 6000 at 99°. Besides a major peak, 2-cyclopropylethanol, there appeared three very small peaks, one of which was found to be cyclopropylmethylcarbinol based on its retention time. Two remaining very minor peaks ($<2\%$ of total area) were neither cyclopentanol nor cyclobutylcarbinol and their structures could not be ascertained. The reaction product of vinylcyclohexane (**2**, commercial product, $>99\%$ pure) was analyzed on a Carbowax 6000 column at 183°. In the case of spiro[2.5]oct-4-ene (**3**), the resulting carbinol mixture was successfully analyzed on a Glycerol column at 120°. Besides two peaks, corresponding to spiro[2.5]octan-4-ol and -5-ol, a broad peak appeared after a far longer retention in the column. This peak corresponded to approximately 12% of total area and could not be characterized.

Isolation and Characterization of the Product.—In runs 1, 2, and 3 (Table I), distillation of the concentrated ether extract gave 2-cyclopropylethanol: bp 140–141°, n^{25}D 1.4328 (lit.[35] n^{25}D 1.4327), 71–82% yield. Its phenylurethan melted at 63.9–64.1° (from low-boiling petroleum ether).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37. Found: C, 70.02; H, 7.27.

β-Naphthalenesulfonate, prepared by the method described by Streitwieser,[36] was successfully purified by a distillation and the fraction boiling at 175–177° (0.03 mm) solidified on standing, mp 26.0–27.0°.

Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.24; H, 5.89.

2-Cyclopropylethanol exhibited characteristic infrared absorptions for cyclopropane at 3080 and 1010 cm^{-1}. In the nmr spectrum, it showed a multiplet at τ 9.33–10.14 (five hydrogens), a quartet at 8.59 (two hydrogens, $J = 7$ cps), a triplet at 6.41 (two hydrogens, $J = 7$ cps), and a singlet at 5.93 (one hydrogen). These results confirmed the 2-cyclopropylethyl structure.

In the hydroboration of vinylcyclohexane (**2**), the main product, 2-cyclohexylethanol, was isolated and derived to the known 3,5-dinitrobenzoate, mp 71.3–71.8° (lit.[8] mp 71–72°).

In run 7 (Table I), a mixture of spiro[2.5]octan-4-ol and -5-ol was isolated in 81.5% yield. The mixture was subjected to a preparative vpc and spiro[2.5]octan-5-ol was collected. Its 3,5-dinitrobenzoate melted at 98.4–99.4°.

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.24; H, 5.04; N, 8.75. Found: C, 56.27; H, 5.21; N, 8.89.

Preparation of Authentic Materials.—Cyclopropylmethylcarbinol was obtained in 42% yield from methylvinylcarbinol[37] *via* the Simmons–Smith reaction: bp 122.5–123.5°, n^{20}D 1.4315 (lit.[38] bp 121–121.5°, n^{21}D 1.4310). Phenylurethan melted at 68.5–69.0°.

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.30; H, 7.44; N, 6.91.

Cyclobutylcarbinol was prepared by the hydroboration of methylenecyclobutane.[39] A fraction boiled at 136–144° (obtained in 58% yield) was a mixture of three compounds, in which cyclobutylcarbinol was a main component (78%). Consequently, cyclobutylcarbinol was purified by the preparative vpc: n^{20}D 1.4438 (lit. bp 140–141°,[40] n^{20}D 1.4440,[41] n^{25}D 1.4430[40]). β-Naphthalenesulfonate melted at 44.0–44.5°.

Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.35; H, 5.88.

Cyclohexylmethylcarbinol was obtained in 67% yield from cyclohexylmagnesium chloride and acetaldehyde: bp 94–97° (28 mm), n^{19}D 1.4667 [lit.[42] bp 82–83° (12 mm), n^{20}D 1.4658].

Registry No.—**1**, 693-86-7; **2**, 695-12-5; **3**, 7647-57-6; spiro[2.5]oct-4-yl xanthate, 7647-58-7; 2-cyclopropylethanol, 2566-44-1; 2-cyclopropylethanolphenylurethan, 7647-59-8; 2-cyclopropylethanol β-naphthalenesulfonate, 7647-60-1; spiro[2.5]octan-5-ol, 7647-61-2; spiro[2.5]octan-5-ol 3,5-dinitrobenzoate, 7647-62-3.

---

(35) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

(36) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957).

(37) A. Wohl and M. S. Losanitoch, *Chem. Ber.*, **41**, 3621 (1908).

(38) R. A. Sneen and A. L. Baron, *J. Am. Chem. Soc.*, **83**, 614 (1961).

(39) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

(40) S. Sarel and M. S. Newman, *ibid.*, **78**, 5416 (1956).

(41) S. Searles, Jr., and E. F. Lutz, *ibid.*, **81**, 3674 (1959).

(42) R. A. Benkeser and J. J. Hazdra, *ibid.*, **81**, 228 (1959).

Proximity Effects. XLV. Solvolyses of Bicyclo[4.2.0]octyl Derivatives[1]

ARTHUR C. COPE,[2] ROBERT W. GLEASON, SUNG MOON,[3] AND CHUNG HO PARK

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received October 17, 1966

Arenesulfonates of six bicyclo[4.2.0]octanols have been solvolyzed in acetic acid and the products have been identified. 3-Cycloocten-1-ol and the bicyclo[4.2.0]octan-7-ols have been shown to be possible intermediates in the formation of *trans*-2-vinylcyclohexanol from the solvolysis of various cyclooctane derivatives.

The bicyclo[4.2.0]octane system has been of interest to us because some of the products obtained from reactions of medium-ring compounds have been derived from intermediates possessing that carbon skeleton. An example is *trans*-2-vinylcyclohexanol, which has been isolated from the solvolyses of *cis,cis*-1,5-cyclooctadiene,[4] *cis*-cyclooctene oxide,[5] and 3-cycloocten-1-yl brosylate.[6] We here report a study of the solvolyses of the arenesulfonates of six bicyclo[4.2.0]octanols. Throughout the paper the *exo* and *endo* isomers of bicyclo[4.2.0]octan-7-ol, bicyclo[4.2.0]octan-2-ol, and bicyclo[4.2.0]octan-3-ol will be referred to as *exo*-**1** and *endo*-**1**, *exo*-**2** and *endo*-**2**, and *exo*-**3** and *endo*-**3**, respectively.

The brosylate of *exo*-**1** was unstable at room temperature and rearranged to *trans*-2-vinylcyclohexyl brosylate on standing for a few minutes. The tosylate of *exo*-**1** was solvolyzed at room temperature in glacial acetic acid–sodium acetate and the solvolysis products after saponification and separation by gas chromatography were found to be *trans*-2-vinylcyclohexanol (48%), *exo*-7-norcaranemethanol[7] (21%), and *exo*-**1**

---

(1) Supported in part by a research grant (NSF-GP-1587) from the National Science Foundation.

(2) Deceased.

(3) To whom inquiries should be addressed at Department of Chemistry, Adelphi University, Garden City, N. Y. 11530.

(4) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).

(5) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957).

(6) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

(7) A. C. Cope and J. A. Meschino, to be published.