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]

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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**

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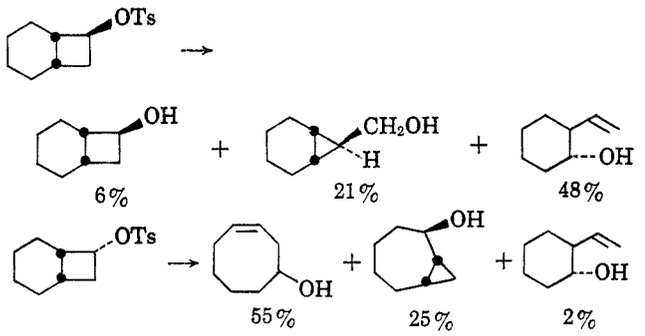
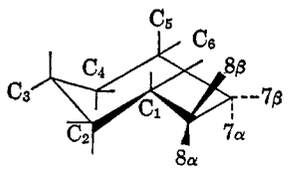
(3) To whom inquiries should be addressed at Department of Chemistry, Adelphi University, Garden City, N. Y. 11530.
(4) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).
(5) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957).
(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.

(6%). The tosylate of *endo*-**1** was inert to acetic acid–sodium acetate at room temperature and required heating at 60° for several hours for complete solvolysis. The products were *trans*-2-vinylcyclohexanol (2%), *exo*-bicyclo[5.1.0]octan-2-ol[8] (25%), and 3-cyclooctenol (55%) (see Scheme I). No *endo*-bicyclo[5.1.0]octan-2-ol was present.

SCHEME I



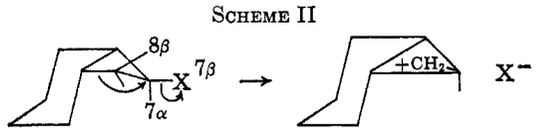
These results should be considered in terms of the most probable conformation of the bicyclo[4.2.0]octane system (A), pictured below. The cyclobutane ring



A

is puckered so that substituents are not eclipsed. The substituents labeled 7β and 8β occupy the *exo* positions; those labeled 7α and 8α occupy the *endo* positions. The 8α and 7β substituents are pseudo-equatorial. The molecule can, of course, flip to an equivalent conformation in which pseudo-equatorial groups become pseudo-axial and *vice versa* as in the similar case of *cis*-decalin. Only a pseudo-equatorial substituent is in a position to depart with its pair of electrons permitting rearrangement to a cyclopropylcarbinyl cation (Scheme II). In the resulting cation the positively charged

SCHEME II

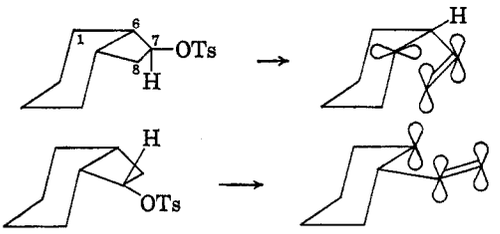


carbon atom is up and the 7α hydrogen atom is down. Thus *exo*-norcaranemethanol would be an expected product from *exo*-bicyclo[4.2.0]oct-7-yl tosylate, and it is found. (It is also known, as would be predicted, that solvolysis of *exo*-norcarancarbinyl tosylate gives *exo*-**1** and none of the *endo* isomer.[7]) Conceivably, the tosylate of *endo*-**1** (the conformer with its *p*-toluenesulfonyl group in a pseudo-equatorial position, 8α in A) could also give this type of rearrangement, but that it does not is no surprise considering that the product would be the highly hindered *endo*-7-norcaranemethanol.

(8) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962).

The fact that *trans*-2-vinylcyclohexanol is formed in high yield from *exo*-**1** tosylate but not from the *endo* isomer is accommodated by the following considerations (see Scheme III). Breaking of the C_1–C_8 bond at C_1 in the *exo* isomer to give the 2-vinylcyclohexyl cation occurs with the potential vinyl group in the pseudo-axial position required for maximum π-orbital overlap. The geometry of this cation may be compared with that of 7-norbornyl cation. However, the conformer of the *endo* isomer having a pseudo-equatorial *p*-toluene-

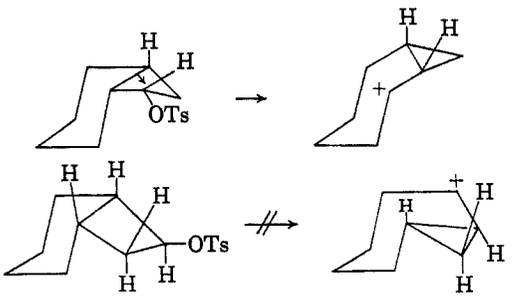
SCHEME III



sulfonyl group has the potential vinyl group also in a pseudo-equatorial position unfavorable for π overlap. This p–π system may be compared with that in the 3-cyclopentenyl cation. Thus the yield of *trans*-2-vinylcyclohexanol from solvolysis of *endo*-**1** tosylate is very low.

The third course of reaction available to the two pseudo-equatorial conformers is the breaking of the C_1–C_6 bond to form a bicyclo[5.1.0]oct-2-yl cation. That only *endo*-**1** tosylate gave a product having this ring system is understandable when one realizes that any such product from the *exo*-tosylate would have to be *trans* fused (Scheme IV).[9]

SCHEME IV



Similar solvolysis products were obtained by Goering and Nelson[10] from homologous compounds, bicyclo[3.2.0]hept-6-yl tosylates (Scheme V).

It is noteworthy that the smaller homologous compound gives somewhat different solvolysis products. McDonald and Reinke[11] obtained the following products from *exo*-bicyclo[2.2.0]hex-2-yl tosylate (Scheme VI).

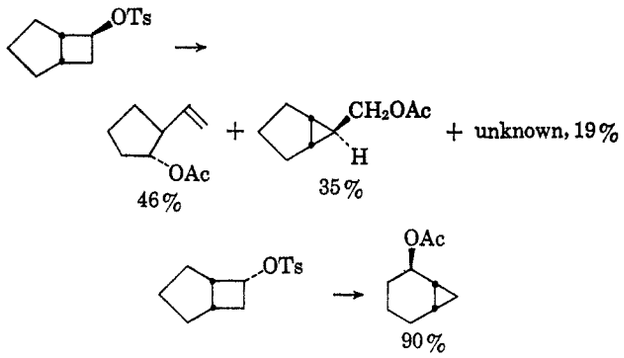
The formation of *endo*-bicyclo[4.2.0]octan-7-ol (*endo*-**1**) and *trans*-2-vinylcyclohexanol from the solvolysis of *cis*-cyclooctene oxide was believed to proceed through

(9) On stereoelectronic grounds the *endo* isomer would be expected to result from the attack of solvent on the bicyclo[5.1.0]oct-2-yl cation,[4] but after hydrolysis of the solvolysis products *exo*-bicyclo[5.1.0]octan-2-ol and 3-cyclooctenol were the products isolated. It seems most probable that these resulted from rearrangement of intially formed *endo* acetate.

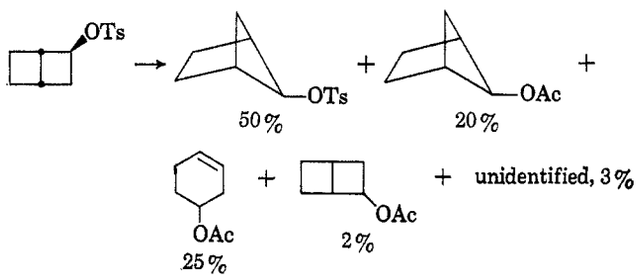
(10) F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.

(11) R. N. McDonald and C. E. Reinke, *J. Am. Chem. Soc.*, **87**, 3021 (1965).

SCHEME V



SCHEME VI



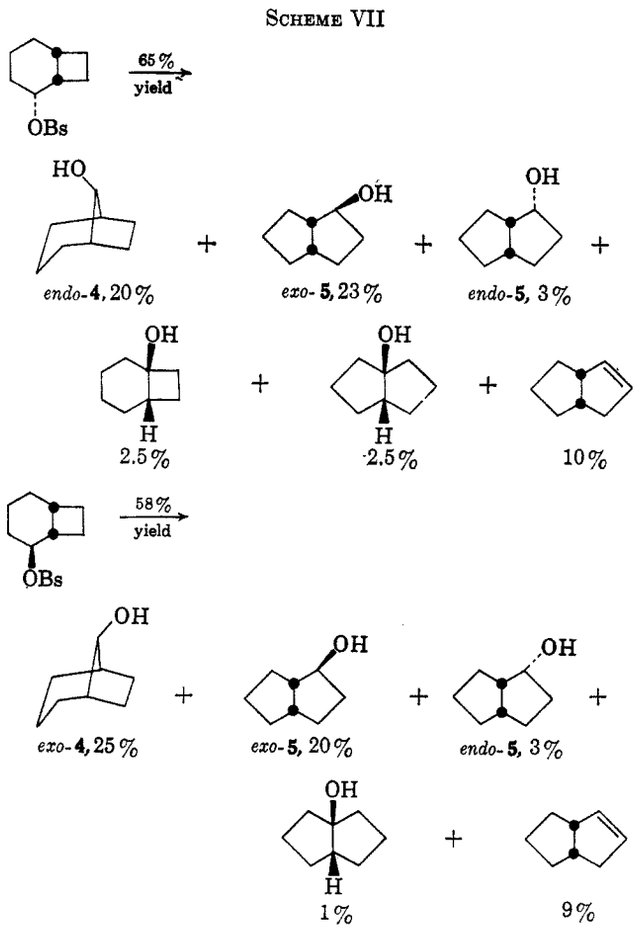
the intermediacy of 3-cyclooctene-1-ol.[4,5,8] To provide some documentation for this hypothesis, the latter was solvolyzed in formic acid under the same conditions used for *cis*-cyclooctene oxide. The products after saponification were *trans*-2-vinylcyclohexanol (22%) and *endo*-**1** (3%); 75% of the starting alcohol was recovered. Solvolysis of *endo*-**1** under these conditions yielded a mixture of *trans*-2-vinylcyclohexanol (46%), 3-cyclooctene-1-ol (37%), two unidentified alcohols (4 and 5%), and unchanged starting alcohol (8%). *exo*-Bicyclo[4.2.0]octan-7-ol (*exo*-**1**), on the other hand, gave only *trans*-2-vinylcyclohexanol; none of the starting alcohol was recovered. These results support the aforementioned hypothesis and also explain why *exo*-**1** was not found among the solvolysis products of *cis*-cyclooctene oxide.

endo-Bicyclo[4.2.0]oct-2-yl brosylate (*endo*-**2** brosylate) was solvolyzed in refluxing acetic acid–sodium acetate for 3 hr. Solvolysis of the *exo* isomer required more drastic conditions; it was treated with acetic acid–sodium acetate in a sealed tube at 150° for 3 days. The results (after saponification of the solvolysis products) are summarized in Scheme VII.

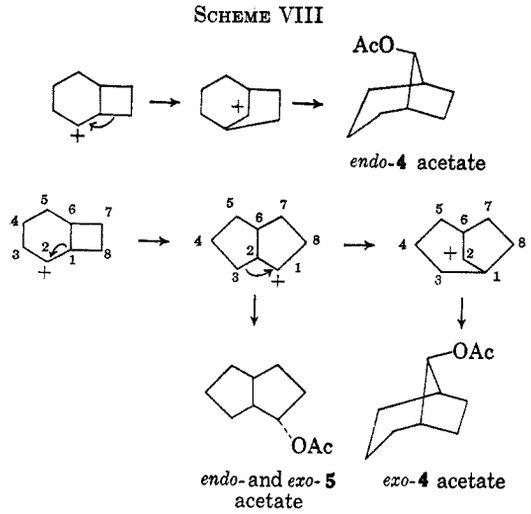
The stereospecific formation of the bicyclo[3.2.1]-octan-8-ols (*exo*- and *endo*-**4**) is noteworthy. The simplest pathway for the formation of *endo*-**4** from *endo*-bicyclo[4.2.0]oct-2-yl brosylate is migration of the C_1–C_8 bond with concerted attack by acetate ions. Such a one-step rearrangement would give the *endo* configuration of bicyclo[3.2.1]oct-8-yl acetate. The *exo* brosylate must rearrange by migration of the C_1–C_6 bond followed by migration of the C_2–C_3 bond and attack by acetate ions to give *exo*-bicyclo[3.2.1]oct-8-yl acetate, as shown in Scheme VIII. It is not obvious from studies of molecular models why each brosylate follows one pathway exclusively. In this regard, it is noteworthy that Woodward and Foote[12] obtained only the *exo* isomer of bicyclo[3.2.1]oct-7-yl acetate

(12) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

SCHEME VII



SCHEME VIII

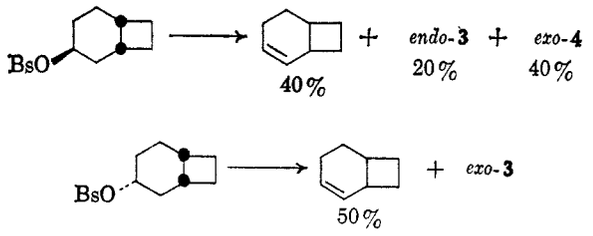


from the solvolysis of *endo*- and *exo*-bicyclo[3.2.1]-oct-8-yl tosylate. In order to test the possibility that the *endo* isomer might have been initially formed from the *exo*-**2** brosylate and subsequently converted to the *exo* acetate, the *endo*-**4** acetate was subjected to the solvolysis conditions of the *exo*-**2** brosylate. It was recovered essentially unchanged.

Only the *endo*-**2** brosylate gave a product of 1,2-hydride shift, bicyclo[4.2.0]octan-2-ol. This is reasonable since the leaving group and the migrating hydrogen atom are trans in the *endo* brosylate, which leads to a more favorable transition state.

The brosylates of *exo*- and *endo*-bicyclo[4.2.0]-octan-3-ol (*exo*-**3** and *endo*-**3**) were each solvolyzed in

SCHEME IX



glacial acetic acid–sodium acetate at 150° for 20 hr. The results are summarized in Scheme IX. Simple substitution with inversion of configuration was a major pathway in both cases.[13] The formation of *exo*-bicyclo[3.2.1]octan-8-ol (*exo*-**4**) from *exo*-**3** brosylate may be pictured as a 1,2-hydride shift from C_2 followed by rearrangement to the product. It is not clear why this product is not also formed from *endo*-**3** brosylate, or why *endo* alcohol **4** is not formed from *exo*-**3** brosylate. The carbonium ion resulting from *exo*-**3** brosylate by 1,2-hydride shift from C_2 would correspond to the carbonium ion derived from *endo*-**2** brosylate. Solvolysis of the latter yielded only the *endo* isomer of the bicyclo[3.2.1]octan-8-ol (**4**).

Experimental Section[14]

Tosylates and Brosylates.—The tosylates and brosylates were prepared from the corresponding bicyclo[4.2.0]octanols.[15] In a typical preparation a cold solution of the bicyclo[4.2.0]octanol in pyridine was added to a cold solution of the arenesulfonyl chloride (2 molar equiv) in pyridine. The solution was allowed to stand in a refrigerator overnight, and the excess arenesulfonyl chloride was hydrolyzed with a small portion of water, while the temperature was kept below 20°. Additional water was then added (three times the volume of pyridine) and the mixture was extracted with ether. The ether extracts were washed with cold 6 *N* hydrochloric acid, water, 5% sodium bicarbonate solution, and water, and dried over magnesium sulfate. After removal of ether, the crude arenesulfonate was recrystallized twice from pentane at −70°. Essential data are summarized in Table I.

TABLE I

ARENESULFONATES OF BICYCLO[4.2.0]OCTANOLS

Arenesulfonate	Mp, °C	Anal., [a]Found, % C	H
exo-**1** tosylate	44.5–46.5	64.32	7.02
endo-**1** tosylate	40.0–41.5	64.18	7.25
exo-**2** brosylate[b]	121.8–123.6[c]	48.65	5.09
endo-**2** brosylate	50.5–51.0	48.79	5.05
exo-**3** brosylate	43.5–44.5	48.89	4.96
endo-**3** brosylate	43.0–44.0	48.87	4.72

[a] Calcd for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19. Calcd for $C_{14}H_{17}O_2BrS$: C, 48.70; H, 4.96. [b] Prepared by J. Martin Grisar and recrystallized from petroleum ether (bp 30–60°). [c] Sealed capillary.

***exo*-Bicyclo[4.2.0]oct-7-yl Brosylate.**—The crude brosylate was recrystallized from pentane, giving white, crystalline material which on standing at room temperature for a few minutes liquefied and turned brown. It solidified after standing at −10° overnight and was recrystallized from pentane yielding white needles, mp 59–60°. This solid was identified as *trans*-2-vinylcyclohexyl brosylate by mixture melting point and by comparison of its infrared spectrum with that of an authentic sample.

The original pentane mother liquors on concentration and cooling to −70° yielded a white solid. After several low-temperature recrystallizations using a jacketed Craig tube and taking care always to maintain the temperature of the crystals and the solutions well below room temperature, *exo*-**1** brosylate, mp 47–49°, was obtained.

Anal. Calcd for $C_{14}H_{17}BrO_3S$: C, 48.70; H, 4.96. Found: C, 48.46; H, 5.05.

Solvolysis of *exo*-Bicyclo[4.2.0]oct-7-yl Tosylate.—To 4 ml of a cold 0.5 *M* solution of sodium acetate in glacial acetic acid (prepared by adding the calculated amount of anhydrous sodium carbonate to glacial acetic acid) was added 0.28 g of *exo*-**1** tosylate. The mixture was allowed to stand at 0–5° for 1 hr and at room temperature for 2 hr, then was poured into 20 ml of water and extracted three times with ether. The combined ether extracts were washed five times with water, twice with 10% sodium carbonate solution, and twice with saturated sodium chloride solution, and dried over magnesium sulfate. The ether was removed by distillation and the residue was passed through a column of acid-washed alumina (eluted with pentane–ether) and then was stirred for 6 hr at room temperature with a solution of 0.1 g of potassium hydroxide in 1 ml of water and 3 ml of methanol. The mixture was extracted four times with ether and the combined ether extracts were washed twice with saturated sodium chloride solution and dried over magnesium sulfate. Removal of the ether gave 0.096 g (75%) of a yellow oil. The mixture consisted of three compounds, isolated by gas chromatography (silicone oil, 165°) and identified as *trans*-2-vinylcyclohexanol (48%), *exo*-7-norcaranemethanol (21%), and *exo*-bicyclo[4.2.0]octan-7-ol (6%).

Solvolysis of *endo*-Bicyclo[4.2.0]oct-7-yl Tosylate.—A solution of 0.56 g of *endo*-**1** tosylate in 8 ml of 0.5 *M* sodium acetate in glacial acetic acid was heated at 60° for 2.5 days. The mixture of products (0.207 g, 82%) was isolated as described for the solvolysis of *exo*-**1** tosylate. The products were isolated by gas chromatography (TCEP, 140°) and identified as *trans*-2-vinylcyclohexanol (2%), *exo*-bicyclo[5.1.0]octan-2-ol (25%), and 3-cycloocten-1-ol (55%).

Solvolysis of *endo*-Bicyclo[4.2.0]oct-2-yl Brosylate.—A solution of 0.62 g of *endo*-**2** brosylate in 6 ml of 0.5 *M* sodium acetate in glacial acetic acid was refluxed for 3 hr. The products (150 mg, 65%) were isolated as described for the solvolysis of *exo*-**1** tosylate, except that the potassium hydroxide treatment was replaced by treatment with lithium aluminum hydride in ether at room temperature. The products, isolated by gas chromatography (silicone oil at 140° and TCEP at 140°), were identified as *endo*-bicyclo[3.2.1]octan-8-ol (*endo*-**4**, 20%), *endo*- (3%) and *exo*-bicyclo[3.3.0]octan-2-ol (23%), bicyclo[4.2.0]octan-1-ol (2.5%), *cis*-bicyclo[3.3.0]octan-1-ol (2.5%), and *cis*-bicyclo[3.3.0]oct-2-ene (10%). An unidentified hydrocarbon was also present (4%).

Solvolysis of *exo*-Bicyclo[4.2.0]oct-2-yl Brosylate.—A solution of 0.58 g of *exo*-**2** brosylate in 5 ml of 0.5 *M* sodium acetate in glacial acetic acid was heated in a sealed tube at 150° for 3 days. (The brosylate was recovered unchanged on heating at 100° for 2 hr.) The mixture of products (150 mg), isolated as described for the solvolysis of *endo*-**2** brosylate, was separated by gas chromatography (TCEP, 150°) and the products were identified as *exo*-**4** (25%), *endo*- (3%) and *exo*-bicyclo[3.3.0]octan-2-ol (20%), *cis*-bicyclo[3.3.0]octan-1-ol (1%), and bicyclo[3.3.0]oct-2-ene (15%).

Solvolysis of *endo*-Bicyclo[4.2.0]oct-3-yl Brosylate.—A solution of 1.05 g of *endo*-**3** brosylate in 10 ml of 0.5 *M* sodium acetate in glacial acetic acid was heated for 20 hr at 150°. Following the work-up described for the solvolysis of *exo*-**1** tosylate up to the potassium hydroxide step, 400 mg of a mixture of bicyclo[4.2.0]oct-2-ene[16] (50%, isolated by gas chromatography on silicone oil at 100°) and an acetate (50%) was obtained. Lithium aluminum hydride reduction of the acetate yielded *exo*-**3**, isolated by gas chromatography (TCEP, 120°).

Solvolysis of *exo*-Bicyclo[4.2.0]oct-3-yl Brosylate.—A solution of 0.65 g of *exo*-**3** brosylate in 7 ml of 0.5 *M* sodium acetate in glacial acetic acid was heated at 150° for 20 hr. Treatment as described for the solvolysis of *endo*-**3** brosylate gave 280 mg of a

(13) Since *exo*- and *endo*-**3** were not separable by gas chromatography, the possibility of the presence of a few per cent of the other isomer in each case cannot be excluded.

(14) Melting points were taken on a Kofler hot stage and are corrected. Analyses were performed by Dr. S. M. Nagy and his associates. Footnote 24 of reference 3 describes the conditions and equipment used for gas chromatography. All identifications of products were made by comparison of retention times and infrared spectra with those of authentic specimens.

(15) A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, **84**, 1928 (1962).

(16) A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *ibid.*, **84**, 4865 (1962).

mixture of bicyclo[4.2.0]oct-2-ene[12] (40%, isolated by gas chromatography on silicone oil at 100°) and two acetates. Reduction with lithium aluminum hydride in ether gave *exo*-bicyclo[3.2.1]octan-8-ol (*exo*-**4**, 20%) and *endo*-**3** (40%), isolated by gas chromatography (TCEP, 90°).

Solvolysis of 3-Cycloocten-1-ol.—A solution of 80 mg of 3-cycloocten-1-ol in 1 ml of 90% formic acid was heated on a steam cone for 2.5 hr. The cooled mixture was diluted with 10 ml of water and extracted with ether. The ether extracts were washed with water and concentrated, then refluxed with 20% sodium hydroxide in methanol–water for 3 hr. The mixture was extracted with ether and the ether layers were washed with water and dried over magnesium sulfate. Removal of the solvent under nitrogen at atmospheric pressure yielded a mixture of 3-cycloocten-1-ol (50%) and *trans*-2-vinylcyclohexanol (50%), isolated by gas chromatography (silicone oil, 135°).

In another run conducted on a larger scale under the same conditions (starting with 500 mg of 3-cycloocten-1-ol), a mixture containing 75% of 3-cycloocten-1-ol, 3% of *endo*-bicyclo[4.2.0]-octan-7-ol, and 22% of *trans*-2-vinylcyclohexanol was obtained. The components were isolated from a TCEP column at 140°.

Solvolysis of *endo*-Bicyclo[4.2.0]octan-7-ol.—*endo*-Bicyclo-[4.2.0]octan-7-ol (160 mg) in 2 ml of 90% formic acid was heated on a steam cone for 2.5 hr. The cooled mixture was diluted with 4 ml of water and extracted with ether. The ether extracts were washed with water, 5% sodium carbonate solution, water, and saturated sodium chloride solution. After drying (magnesium sulfate), the solvent was removed and the residue was saponified with 2 ml of 15% sodium hydroxide in methanol–water at room temperature for 24 hr. The mixture was diluted with 4 ml of water and extracted with ether. The ether extracts were washed with water and saturated sodium chloride solution, and dried over magnesium sulfate. Removal of the solvent yielded 100 mg of a mixture containing *trans*-2-vinylcyclohexanol (46%), *endo*-**1** (8%), 3-cycloocten-1-ol (37%), and two unidentified alcohols (4 and 5%), isolated from a TCEP column at 140°. The unidentified alcohols are believed to be derived from *trans*-2-vinylcyclohexanol by migration of the double bond. Both had retention times similar to that of *trans*-2-vinylcyclohexanol; the infrared spectrum of each showed the presence of a double bond.

Solvolysis of *exo*-Bicyclo[4.2.0]octan-7-ol.—*exo*-Bicyclo[4.2.0]-octan-7-ol (80 mg) was solvolyzed in 1 ml of 90% formic acid according to the procedure described for the *endo* isomer. The product (70 mg) was homogeneous on gas chromatography (TECP at 140°), and was identified as *trans*-2-vinylcyclohexanol.

Thermal Stability of *endo*-Bicyclo[3.2.1]oct-8-yl Acetate.—A solution of 0.5 g of *endo*-bicyclo[3.2.1]oct-8-yl acetate in 5 ml of 0.5 *M* sodium acetate in glacial acetic acid was heated in a sealed tube at 150° for 3 days. The product, isolated as described for the solvolysis of *endo*-**2** brosylate, was found to be the unchanged acetate. The product was homogeneous on gas chromatography (TCEP) and the infrared spectrum of the collected sample was superimposable on the spectrum of an authentic sample of the acetate.

Registry No.—*exo*-**1** tosylate, 7604-67-3; *endo*-**1** tosylate, 7604-68-4; *exo*-**2** brosylate, 7604-69-5; *endo*-**2** brosylate, 7604-70-8; *exo*-**3** brosylate, 7604-71-9; *endo*-**3** brosylate, 7604-72-0; *exo*-**1** brosylate, 7604-73-1; *exo*-bicyclo[4.2.0]oct-7-yl brosylate, 7604-74-2; *exo*-bicyclo-[4.2.0]oct-7-yl tosylate, 7604-75-3; *endo*-bicyclo[4.2.0]-oct-7-yl tosylate, 7604-76-4; 3-cycloocten-1-ol, 4114-99-2; *endo*-bicyclo[4.2.0]octan-7-ol, 7604-78-6; *exo*-bicyclo[4.2.0]octan-7-ol, 7604-79-7.

The 2,3-Diphenyl-1,4-dioxane Isomers

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2,3-Bis(4-bromophenyl)-1,4-dioxane (**4a**) and its 4-chloro counterpart (**4b**) have been converted to 2,3-diphenyl-1,4-dioxane (**1**), mp 42–45°, and to 2,3-bis(4-carboxyphenyl)-1,4-dioxane (**6**). The partial resolution of the latter constitutes unequivocal proof of the *trans* configuration of the lower melting 2,3-diphenyl-1,4-dioxane isomer. The isomer which melts at 136° is therefore *cis*.

A number of recent reports[4] have been concerned with the conformation of the 2,3-dichloro- and the 2,3-diphenyl-1,4-dioxane isomers as deduced from nmr spectra. In all of these reports the configurations assigned to these pairs of isomers as a result of previous work in these laboratories[5] have been assumed to be correct. The configurational assignments for the dichlorodioxanes were based on unequivocal evidence[5a] and they have since been confirmed by X-ray crystallographic studies.[4b] The configurational assignments for the 2,3-diphenyldioxanes were less unequivocally established, but they were nevertheless well based on conventional organic chemical argument.[5b] Another recent report,[6] however, has contended that the assignment of a *cis* configuration to the higher melting 2,3-dichloro-1,4-dioxane[5a] is wrong, and that the assignments for the 2,3-diphenyl-1,4-dioxanes[5b] are correctly those originally proposed.[7]

The arguments presented for these reassignments of configuration[6] are specious at best. A rational analysis of the A_2B_2 nmr spectrum of the higher melting dichlorodioxane isomer[4d,e] has added additional evidence for its *cis* nature, if such be needed, and the claim that the two isomers are both *trans* (noninterconverting axial,axial and equatorial,equatorial conformers) has since been disavowed.[8] There has been no disavowal of the reversal of the configurational assignments for the diphenyldioxane isomers,[6] however. The question of the correctness of our earlier assignments[5b] for these isomers needs to be laid to rest.

We report here unequivocal evidence that the lower melting diphenyldioxane isomer (46°, **1**) has a *trans* configuration, whence by inference the higher melting isomer (136°, **2**) must have a *cis* configuration. A very recent analysis of the A_2B_2 nmr spectrum of **2** serves to confirm the *cis* nature of the latter isomer.[4f]

The evidence that **1** has a *trans* configuration is summarized in Chart I.

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