the usual manner of 11β,21-dihydroxy-16α,17α-isopropylidenedioxy-6α-methyl-4-pregnene-3,20-dione (XVIIIa)[16] gave the 21-acetate (crystallized from acetone–petroleum ether), m.p. 218–219°, $[\alpha]^{25}D$ + 131°, λ_{max} 242 mμ (ϵ 14,100); ν_{max} 3390, 1760, 1730, 1668, 1612, 1374, 1093, 1055 and 862 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{38}O_7$ (474.57): C, 68.33; H, 8.07. Found: C, 67.93; H, 8.19.

16α,21-Diacetoxy-17α-hydroxy-6α-methyl-4-pregnene-3,11,20-trione (XXb).—To a previously prepared mixture of 800 mg. of chromic anhydride in 10 ml. of pyridine was added a solution of 1.25 g. of 16α,21-diacetoxy-11β,17α-dihydroxy-6α-methyl-4-pregnene-3,20-dione (XIV) in 20 ml. of pyridine. The mixture was allowed to stand at room temperature for 20 hours with occasional stirring after which methanol was added and the solvents were evaporated. The residue was extracted with ethyl acetate, washed with dilute sulfuric acid, dilute sodium bicarbonate and finally with water to neutrality. After drying and evaporation the residue was crystallized from acetone–petroleum ether to yield 630 mg. of white solid, m.p. 201–202°. A small portion was crystallized several times from acetone–petroleum ether to give pure XXb, m.p. 207–208°, $[\alpha]^{25}D$ +123°, λ_{max} 238 mμ (ϵ14,900); ν_{max} 3450, 1754, 1712, 1674, 1612 and 1232 cm.$^{-1}$

Anal. Calcd. for $C_{26}H_{34}O_8$ (474.55): C, 65.80; H, 7.22. Found: C, 65.54; H, 7.21.

16α,17α,21-Trihydroxy-6α-methyl-4-pregnene-3,11,20-trione (XXa).—To a solution of 604 mg. of the 16,21-diacetate XXb in 80 ml. of methanol was added 2.0 ml. of 10% aqueous potassium carbonate and the mixture was agitated at room temperature with a stream of nitrogen for 20 minutes. After the addition of 1.0 ml. of glacial acetic acid and evaporation to one-third volume, water was added and 350 mg. of white needles, m.p. 236–237°, were filtered. Crystallization of a portion twice from acetone–petroleum ether gave the pure triol XXa, m.p. 236–238°, λ_{max} 238 mμ (ϵ 15,00), $[\alpha]^{25}D$ +148° (pyridine); ν_{max} 3420, 3300, 1710, 1658 and 1612 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{30}O_6$ (390.46): C, 67.67; H, 7.74. Found: C, 67.81; H, 7.91.

21-Acetoxy-16α,17α-isopropylidinedioxy-6α-methyl-4-pregnene-3,11,20-trione (XXI).—A solution of 245 mg. of the triol-trione XXa in 12 ml. of acetone and 0.025 ml. of 70% perchloric acid was stirred at room temperature for 2.5 hours after which 0.4 ml. of saturated sodium bicarbonate and 5 ml. of water were added. Extraction with ethyl acetate and evaporation gave 270 mg. of oil which resisted all attempts to induce crystallization. Chromatography resulted again in an intractable oil. This oil (190 mg.) was acetylated to give 160 mg. of white solid, m.p. 212–214°, from acetone–petroleum ether. Two additional crystallizations from the same solvent pair gave the pure acetonide XXI, m.p. 214–216°, λ_{max} 236 mμ (ϵ 16,000), $[\alpha]^{25}D$ +183°; ν_{max} 1754, 1730, 1708, 1672, 1610 and 862 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{36}O_7$ (472.56): C, 68.62; H, 7.68. Found: C, 68.51; H, 7.82.

PEARL RIVER, N. Y.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Some 2- and 7-Derivatives of Benznorbornene

BY PAUL D. BARTLETT AND WILLIAM P. GIDDINGS

RECEIVED JULY 23, 1959

exo- and *endo* 2-benznorbornenol, *anti*-7-benznorbornenol and *anti*-7-benznorbornadienol (II, IV, VII and IX, respectively) have been prepared and the rates of acetolysis of their *p*-bromobenzenesulfonates have been measured for comparison with the esters of the corresponding norborneols and norbornenols. All four esters undergo acetolysis without rearrangement. The results are shown in Tables I and II. Compared with the C–C double bond, the fused benzene ring has a similar effect on the 2-bromobenzenesulfonates, but it provides only about half (on an energy scale) of the large assistance to ionization at C_7 which the double bond offers. The additional double bond in the *p*-bromobenzenesulfonate of IX favors ionization by a factor of 100.

Introduction

Wittig's elegant procedure[1] for the addition of dehydrobenzene (benzyne) to dienes has made readily available benznorbornadiene (I) from which the benzo analogs of *endo*-, *exo*- and 7-norbornenol can be prepared. These compounds are of special interest in view of the extraordinary spread of reactivities observed in the solvolysis of the sulfonate esters of 2- and 7-norborneol and norbornenol. Figure 1 summarizes the reported rate constants relative to the corresponding cyclohexyl ester at 25°. The high driving force for ionization of *exo*-2-norbornenyl *p*-bromobenzenesulfonate is associated with homoallylic delocalization of the π-electron pair in the double bond and leads to a rearranged product. The much greater driving force observed in *anti*-7-norbornenyl *p*-bromobenzenesulfonate has been attributed to delocalization of the same electron pair among the three centers represented by carbon atoms 5, 6 and 7, but this ionization leads to a product in which both structure and configuration have been fully retained.

In the S_N1 reactions of allylic and benzylic compounds, the benzene ring affords a driving force between those of the vinyl and 1-propenyl groups. For example, from rate constants in the literature, α-phenylethyl chloride undergoes ethanolysis at 25° in absolute alcohol at a first-order rate about 3.5 times that of α-methylallyl chloride,[2-4] but a thousand times more slowly than α, γ-dimethylallyl chloride.[5]

Since allylic delocalization is entirely by π-interactions, while homoallylic delocalization depends strongly upon oriented σ-overlap of orbitals,[6,7] it was of special interest to compare the effects of the benzene ring fused at 5,6 with those of the double bond in the same position.

Preparation of Compounds.—The flow sheet summarizes the preparations starting with benznorbornadiene prepared by the method of Wittig and Knauss. As expected, direct hydration of the double bond led to *exo*-2-benznorbornenol, m.p. 74.1–75.4°, which could be oxidized to the corre-

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[1] G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

[2] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

[3] W. G. Young and L. J. Andrews, THIS JOURNAL, **66**, 421 (1944).

[4] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

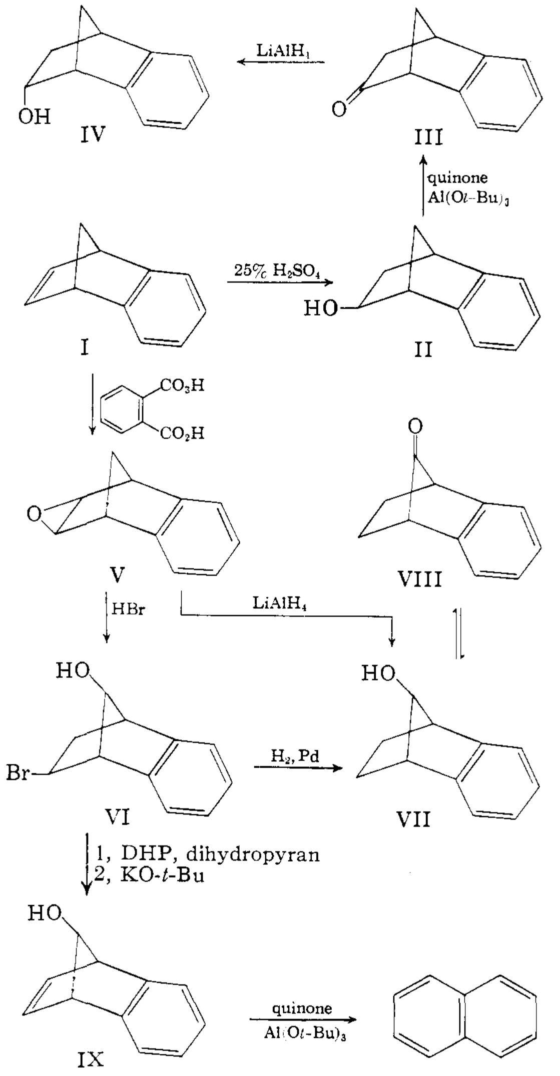
[5] H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

[6] M. Simonetta and S. Winstein, *ibid.*, **76**, 19 (1954).

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

sponding ketone (yellow 2,4-dinitrophenylhydrazone, m.p. 175.4–177.0°). Lithium aluminum hydride reduction of this ketone yielded *endo*-2-benznorbornenol. The *endo*-benznorbornenol melted at 74.5–75.4°, but was readily distinguished from the *exo* isomer by its *p*-bromobenzenesulfonate, m.p. 135.1–136.1°, in contrast to that of the *exo*-alcohol, m.p. 82.2–84.4°, as well as by the infrared spectra. Benznorbornadiene is readily oxidized by monoperphthalic acid to a single epoxide, m.p. 26–29°, whose behavior on reaction with hydrogen bromide is parallel to that of epoxynorbornane. Addition of HBr occurs with rearrangement producing *exo*-2-bromo-*anti*-7-benznorbornenol, m.p. 135.3–136.8°, which can be converted into *anti*-7-benznorbornenol, m.p. 105.6–107.1° by reduction with hydrogen-on-palladium or into *anti*-7-benznorbornadienol, m.p. 106.3–108.2°, by treatment of the dihydropyran derivative with potassium *t*-butoxide. 7-Benznorbornenol can be oxidized by the Oppenauer method to 7-benznorbornenone (principal carbonyl absorption at 5.58 mμ; 2,4-dinitrophenylhydrazone, m.p. 143.6–146.4°), but no way has been found to convert this into *syn*-7-benznorbornenol. In the case of *anti*-7-benznorbornadienol, attempts to produce a ketone by even the mildest procedures led only to the formation of naphthalene with loss of the 7-carbon atom.

FLOW SHEET



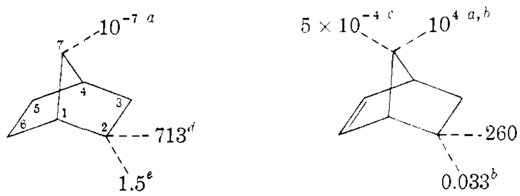


FIG. 1. Reported solvolytic reactivities (Relative to cyclohexyl) of 2- and 7-*p*-bromobenzenesulfonates of norbornane and norborene.

[a] S. Winstein, M. Shatavsky, C. J. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955). [b] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956). [c] S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957). [d] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952). [e] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

Rearrangement of the epoxide occurred not only on addition of hydrogen bromide but also on heating under reflux with lithium aluminum hydride in ether. The product isolated by crystallization and chromatography melted at 103.0–104.6° and was identified by its infrared spectrum as *anti*-7-benznorbornenol. This reaction has also been observed by Meinwald and Lewis.[8]

Solvolysis of *p*-Bromobenzenesulfonates.—Solvolysis of the brosylates of *endo*- and *exo*-2-benznorbornenols in glacial acetic acid containing equivalent sodium acetate yielded the same acetate in each case, which was reduced by lithium aluminum hydride to *exo*-2-benznorbornenol. Solvolysis of *anti*-7-benznorbornenyl brosylate yielded *anti*-7-benznorbornenyl acetate while *anti*-7-benznorbornadienyl brosylate yielded *anti*-7-benznorbornadienyl acetate. Both of these acetates were reduced by lithium aluminum hydride to *anti*-7-benznorbornenol. *anti*-Benznorbornadienyl acetate also was prepared by acetylation of the alcohol and reconverted to the latter by methylmagnesium iodide.

The solvolysis rates of the four *p*-bromobenzenesulfonates are summarized in Table I together with the derived activation parameters. For purposes of comparison with related compounds, the rate constants at 25° have been calculated in each case using extrapolation in those cases where the rate was not measured directly at that temperature. Table I shows a comparison of the rates here determined with those for related compounds measured by others. In the *endo*-2-brosylate the rate is slower than that of *endo*-norborneol by a factor of about 250 and is about five times slower than in *endo*-2-norbornenyl brosylate. The ratio of solvolysis rate constants for the *exo* and *endo* isomers is 5000, in the same range as the corresponding ratio in the 2-norborneneyl brosylates.

In the 7 series the disparity is much greater between the effect of the fused benzene ring and that of the double bond. *anti*-7-Benznorbornenyl brosylate undergoes solvolysis at a rate more than

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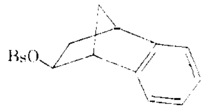
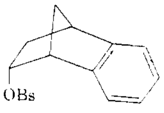
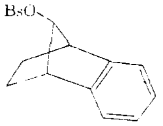
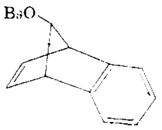
(8) J. Meinwald, private communication.

TABLE I

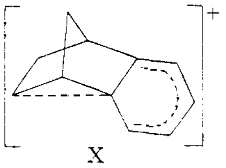
KINETIC DATA FOR BENZNORBORNENYL p-BROMOBENZENESULFONATE ACETOLYSIS IN GLACIAL ACETIC ACID CONTAINING SODIUM ACETATE

Compound	Temp., °C.	$k_1 \times 10^6$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, cal./deg.	Extrapolated k_1, (25°) sec.$^{-1} \times 10^9$	k_1 (25°) relative to		
						Cyclohexyl	Norbornyl analog (CH_2—CH_2 in place of benzo)	Norbornenyl analog ($CH{=}CH$ in place of benzo)
	50.03 ± 0.01 $25.03 \pm .02$	188 ± 18 7.17 ± 0.20	24.1 ± 0.9	-1.2 ± 3.1	7470	43	0.06	0.16
	$114.8 \pm .2$ $95.75 \pm .05$	$54.9 \pm .7$ $7.60 \pm .14$	27.85 ± 1.45	-7.0 ± 3.9	1×10^{-9}	0.006	0.004	0.2
	$95.75 \pm .05$ $74.79 \pm .05$	105.8 ± 3.3 10.22 ± 0.58	27.6 ± 1.1	-2.3 ± 3.0	10	0.06	6×10^5	6×10^{-6}
	$60.00 \pm .05$ $35.00 \pm .05$	161.5 ± 1.5 5.57 ± 0.16	26.85 ± 0.35	4.45 ± 0.95	1200	7.0	1.4×10^4	

five powers of ten less than that reported for *anti*-7-norbornenyl brosylate[9] or for the similarly constituted brosylate derived from dicyclopentadiene.[10] At the same time, if we compare the 7-brosylate having a fused benzene ring with the saturated 7-norbornyl brosylate, the benzene fusion is seen to provide a net driving force amounting to a factor of about 6 × 10^5. The further introduction of the double bond in *anti*-7-benznorbornadienyl brosylate increases the rate of solvolysis by a factor of over 100.

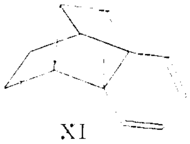
Discussion

In both norbornenyl and benznorbornenyl compounds there is a pair of bond moments (at C_1–C_6 and C_4–C_5) unfavorable to a positive charge at C_2 or C_7. The depression of ionization rate by factors of 44 and 250 in the respective *endo*-2-*p*-bromobenzenesulfonates measures the effect of this sp^2–sp^3 polarization. In correcting for the effect of β-phenyl groups on ionization rate, Winstein and co-workers[11] used a rough factor of 10 per phenyl group. This is consistent with the effects in the bicyclic compounds, where two such moments are present instead of one, and where the aromatic ring resists the strain imposed by the bicycloheptenyl system and keeps the shared carbons using more truly sp^2 orbitals than the simple double bond can do. If this opposition to ionization is cancelled by looking at the *exo*/*endo* ratio, the aromatic ring is seen to be almost identical to the double bond in its ability to assist ionization at the 2-position. The charge delocalization in the structure X would appear as favorable in the benzene ring as in any phenonium ion or any aromatic substitution intermediate.



X

On the other hand, the fused benzene ring is vastly inferior to the double bond in assisting ionization at C_7, providing about 7 instead of 14 kcal. of free energy of activation to the ionization process. Unlike the situation in X, the stabilization in the ion XI develops a realignment of



XI

atomic orbitals which can absorb a double bond completely but which, in benzene, can occur only at the expense of some of the aromatic stabilization energy. This difference is reflected in the results of a simple MO calculation for the 7-benznorbornadienyl cation using the same treatment which Roberts and co-workers applied to the 7-norbornenyl.[7,12]

The hundredfold increase in ionization rate brought about by the double bond in *anti*-7-benznorbornadienyl p-bromobenzenesulfonate occurs despite dipole effects which might tend to produce up to a hundredfold retardation instead. There is accordingly a driving force of the order of 10^4 arising from this structure. The possibility might be considered that some incipient stabilization of the cation occurs at the transition state from the side of the departing group as well as from the opposite side. However, *syn*-7-nor-

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(9) S. Winstein, M. Shatavsky, C. J. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).

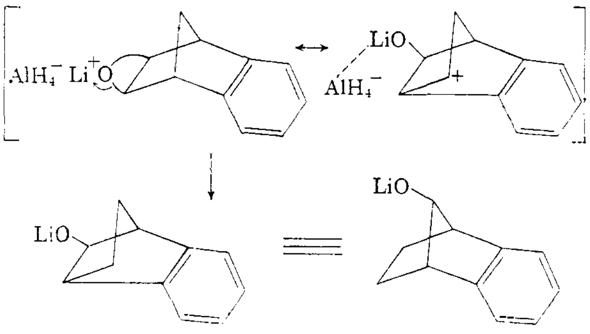
(10) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(11) S. Winstein, B. K. Morse, E. Grunwald, K. Schreiber and J. Corse, THIS JOURNAL, **74**, 1117 (1952).

(12) W. P. Giddings, Thesis, Harvard University, 1959.

bornenyl tosylate,[13] which is accelerated in acetolysis by a factor of 10^4 over the saturated tosylate (and hence has a driving force of about 10^6), does not form the 7-norbornenyl cation. There is no evidence at present to indicate that the front-side assistance in question can be of any importance. One of the suggested explanations for the slow solvolysis of 7-norbornyl esters is the bond angle C_1–C_7–C_4 of probably less than 100°, especially unfavorable for the formation of a trigonal carbonium ion.[7] Because the net effect of the 2,3-double bond is to push C_1 and C_4 farther apart (because of increased C_1–C_2–C_3–C_4 bond angles and in spite of a shortened C_2–C_3 bond distance) it may relieve the constriction of the C_1–C_7–C_4 angle enough to be of real importance.

The rearrangement attending reduction of benznorbornadiene oxide was unexpected in view of cases in which the AlH_4^- ion appears to give normal displacement by an S_N2 mechanism. Its occurrence must be connected both with hindrance to attack at the *endo* side (the epoxide being assumed to be *exo*) and with first attachment of the lithium ion to the epoxy oxygen, permitting an electronic delocalization which is the basis of attack of the hydride at C_1 as in the case of HBr addition.



Still another mechanism of lithium reduction is seen in the ready conversion of 1-bromotriptycene into 1-triptycyllithium by lithium aluminum hydride[14] and by *n*-butyllithium.[15]

Experimental[16]

Benznorbornadiene (I) was prepared by the procedure of Wittig and Knauss,[17] b.p. 88–89° (19 mm.) (reported[1] 82.5–83.0° (12 mm.)).

***exo*-Benznorbornenol** (II).—Benznorbornadiene was heated under reflux for five hours with rapid stirring with four times its weight of 25% sulfuric acid.[18] After cooling, the brown upper layer was dissolved in ether, separated; the aqueous layer extracted three times with ether; the combined organic layers washed with water and with dilute sodium carbonate solution, dried over sodium sulfate, and evaporated. The residue was dissolved in petroleum ether and chromatographed over Merck alumina with petroleum ether until all unreacted benznorbornadiene and a product thought to be di-*exo*-benznorbornadienyl ether were eluted. *exo*-Benznorbornenol was eluted slowly with anhydrous ether and rapidly with 20% absolute ethanol in anhydrous ether, along with a yellow gum which was removed by treatment of the solution with charcoal. Recrystallization from petroleum ether yielded from 10 to 50% of white crystalline product, m.p. 74.1–75.4°. Subsequently, addition of acetic acid to the double bond[19] was found to be a preferable procedure for the preparation of *exo*-norborneol. Standard procedures were used for this sequence. Infrared spectrum of II: 2.79, 3.00, *3.40*, *6.85*, 6.91, 7.00, 7.29, 7.67, 7.78, 7.97, 8.17, 8.44, 8.64, 8.26, 9.19, *9.31*, *9.59*, 9.80, *10.29*, 10.86, 11.07, 11.37, 12.14, 12.84, 13.36, 13.78.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 82.25; H, 7.69.

***exo*-Benznorbornenyl *p*-bromobenzenesulfonate** was prepared in the usual manner,[20] with anhydrous pyridine. Crystals formed directly upon addition of the pyridine solution after two days at room temperature to ice and water. The brosylate was collected by suction filtration and washed repeatedly with water, then dissolved in ether; the solution was washed 3 times with ice-cold dilute hydrochloric acid and twice with cold dilute sodium carbonate solution, and dried over sodium sulfate. The solution was decanted and evaporated to about one-fifth of its volume; then four times the remaining volume of petroleum ether was added and the solution cooled at −25° in a freezer. After several recrystallizations in this manner the brosylate melted at 82.2–84.4°. Pumping in a drying pistol with phosphorus pentoxide caused the brosylate to darken and become infusible; pumping with potassium hydroxide pellets and paraffin shavings gave a white product.

Anal. Calcd. for $C_{17}H_{15}O_3SBr$: C, 53.83; H, 3.96. Found: C, 53.91; H, 4.11.

Structure of Acetolysis Product.—The product from the acetic acid solvolysis for 10 half-lives of *exo*-benznorbornenyl brosylate was diluted with ether and aqueous sodium carbonate solution was added. Solid sodium carbonate was added in small portions until no further bubbling occurred. After washing twice with aqueous sodium carbonate and drying over sodium sulfate, the ether solution was evaporated on the steam-bath and the residue pumped for several hours in a vacuum desiccator. The residue was added dropwise to excess lithium aluminum hydride in ether, causing gentle boiling with each drop, and allowed to stand at room temperature overnight. Water was added cautiously until no further reaction occurred; then 10% sulfuric acid was added until all precipitate had dissolved. The ether layer was separated, washed with sodium carbonate solution and dried over sodium sulfate. Evaporation of the ether left white crystals which had an infrared spectrum identical with that of *exo*-benznorbornenol.

2-Benznorbornenone (III) was prepared in 70% yield by oxidation of *exo*-benznorbornenol with chromium trioxide in pyridine.[21] A more convenient preparation was the following: A solution of 12.70 g. of *exo*-benznorbornenol, 10.0 g. of quinone and 38.3 g. of aluminum *t*-butoxide in 1000 ml. of benzene was heated under reflux for two days. The black solution was extracted twice with dilute sulfuric acid and 5 times with dilute sodium hydroxide solution until the extract was colorless. The benzene solution was dried over sodium sulfate and evaporated and the residue chromatographed over Merck alumina in petroleum ether. With petroleum ether and absolute ether 11.7 g. (90%) of ketone was eluted with the principal carbonyl absorption in the infrared at 5.69 μ with no alcohol detected. Ultraviolet maxima in ethanol were at 210 mμ (log ε 4.03), 264 (2.76), 273 (2.78) and 300 (mμ 2.92); infrared spectrum of III: 3.38, 5.55, *5.69*, 5.83, *6.81*, 7.08, 7.68, 7.87, 8.30, 8.47. 8.72, *8.92*, 9.23, 9.42, 9.88, *10.22*, 10.75, 11.12, 12.28, 12.58, **13.25**, 13.48.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.54; H, 6.33. Found: C, 83.47; H, 6.33.

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[13] S. Winstein and E. T. Stafford, THIS JOURNAL, **79**, 505 (1957).

[14] R. P. Anderson, unpublished work in this Laboratory, 1954.

[15] G. Wittig and U. Schöllkopf, *Tetrahedron*, **3**, 91 (1958).

[16] All melting points were taken with uncalibrated Anschütz thermometers; boiling points are uncorrected. Microanalyses were performed by Dr. S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology. Infrared spectra were taken with a Perkin-Elmer model 21 and ultraviolet spectra with an Applied Physics Corporation Cary recording spectrophotometer.

[17] G. Wittig and E. Knauss, ref. 1. We thank Professor Wittig for kindly supplying the details of this procedure before publication.

[18] H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945).

[19] J. Bertram and H. Walbaum, *J. prakt. Chem., N. F.*, **49**, 1 (1894); H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 1178 (1945); P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956.

[20] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[21] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 427 (1953).

The 2,4-dinitrophenylhydrazone was prepared in the usual manner.[22] After 3 recrystallizations from 95% ethanol, the yellow derivative melted at 175.4–177.0°. The ultraviolet spectrum in ethanol showed maxima at 232 mμ (log ε 4.51) and at 361 mμ (log ε 4.64).

Anal. Calcd. for $C_{17}H_{13}O_4N_4$: C, 60.35; H, 4.14. Found: C, 60.81; H, 4.46.

***endo*-Benznorbornenol (IV).**—To 1.2 g. of lithium aluminum hydride in 40 ml. of ether was added cautiously dropwise 10.10 g. of 2-benznorbornenone. Each drop produced a violent audible momentary reaction. The mixture was refluxed for three hours, cooled and worked up as described above for the acetolysis product of *exo*-benznorbornenyl brosylate. The crude product, 9.41 g. (93%) of white crystals, melted at 61–66° and its infrared spectrum showed the presence of no *exo*-benznorbornenol. After repeated recrystallization from ether–petroleum ether the m.p. was 74.5–75.4°; infrared spectrum of IV: 2.80, *3.37*, 6.85, 6.90, 6.97, *7.20*, 7.48, 7.66, 7.84, 8.08, 8.22, 8.73, 8.85, *8.93*, *9.05*, 9.38, *9.61*, 9.93, 10.27, 10.57, 10.77, 11.20, 12.54, 12.84, *13.33*, 14.13, 14.57.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 82.17; H, 7.35.

***endo*-Benznorbornenyl *p*-bromobenzenesulfonate** melted at 135.1–136.1° after repeated recrystallization from ether–petroleum ether. *Anal.* Calcd. for $C_{17}H_{15}O_3SBr$: C, 53.83; H, 3.96. Found: C, 53.85; H, 3.94. Treatment of the solvolysis product as described above for the *exo* isomer yielded an acetate with an infrared spectrum identical with that of the *exo* product.

Benznorbornadiene Oxide (V).—A solution of 22.2 g. of benznorbornadiene in 375 ml. of 0.437 *N* monoperphthalic acid in ether, prepared by the method of Royals and Harrell,[23] was kept in the refrigerator at about 6° for 7 days, then extracted three times with 20% sodium hydroxide solution, washed twice with water, dried over sodium sulfate, the ether evaporated and 15.5 g. (63%) of benznorbornadiene oxide, m.p. 26–29°, distilled at 97–97.5° (7 mm.); infrared spectrum of V: *3 38*, 5.17, 5.28, *6.83*, 6.91, 7.09, *7.32*, *7.79*, *8.10*, 8.36, 8.40, 8.73, 9.16, 9.21, 9.93, *9.99*, 10.20, 10.50, 10.80, *11.04*, 11.18, 11.52, *11.81*, 12.45, *13.28*, *13.53*, 14.37.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.53; H, 6.33. Found: C, 83.42; H, 6.38.

***exo*-2-Bromo-*anti*-7-benznorbornenol[24] (VI).**—A solution of 15.5 g. of benznorbornadiene oxide in 90 ml. of petroleum ether was cooled to 10° and poured slowly in portions into 20 ml. of 48% hydrobromic acid with shaking and cooling in an ice-bath. The liquid phases were frequently decanted from the copious bluish sticky precipitate and shaken further in a clean flask. The solid was filtered off and dissolved in 400 ml. of ether; the aqueous phase was extracted three times with ether and the combined ethereal solution washed with dilute aqueous sodium carbonate solution and dried over sodium sulfate. The ether solution was then evaporated down to about 50 ml. and 300 ml. of petroleum ether added. After cooling to −25° in the freezer 12.0 g. (51.2%) of bromohydrin, m.p. 127–134°, was collected. After several recrystallizations from ether–petroleum ether the pure product melted at 135.3–136.6°; infrared spectrum of VI: *2.80*, 3.38, *6.83*, 6.95, 7.17, 7.78, 7.89, *8.07*, 8.30, 8.39, 8.51, 8.70, 8.80, 8.95, 9.37, 9.88, 10.39, 11.32, 12.66, 13.15, 13.43, 14.03, 15.40.

Anal. Calcd. for $C_{11}H_{11}OBr$: C, 55.23; H, 4.60. Found: C, 55.63; H, 4.77.

***anti*-7-Benznorbornenol (VII).**—The above bromohydrin was treated with hydrogen in the presence of Baker and Co. 10% palladium-on-charcoal catalyst in absolute ethanol solution. Evaporation of the filtered solution left a black residue which was dissolved in ether, decolorized with charcoal, and evaporated to yield 96% of an alcohol, m.p. 87.6–100° after one recrystallization from ether–petroleum ether, the infrared spectrum of which showed the presence of no *exo* or *endo* isomers. Pure material, m.p. 105.6–107.1°, could be obtained only by chromatography in anhydrous ether over Merck alumina, in the first fraction containing any product.

A solution of benznorbornadiene oxide in ether was heated under reflux for 2 hr. with excess lithium aluminum hydride and worked up in the usual manner. After separation from unreacted epoxide by two recrystallizations from petroleum ether and by chromatography over Merck alumina in ether, *anti*-7-benznorbornenol, m.p. 103.0–104.6°, was identified by the infrared spectrum. To 1.7 g. of lithium aluminum hydride in 40 ml. of ether was added from a dropping funnel 14.9 g. (0.0943 mole) of epoxide, resulting in gentle boiling, and heated on the steam-bath for 5 hr. Workup in the usual manner yielded 14.0 g. of liquid containing a few crystals; the infrared spectrum showed mostly recovered epoxide. This residue was added dropwise with stirring to a refluxing mixture of 2 g. of lithium aluminum hydride in 100 ml. of ether. By the time 21 hr. of refluxing and stirring had elapsed, the ether had evaporated and a gray paste remained. Ether was added and the mixture worked up as usual to yield 13.3 g. (0.0832 mole, 88.2%) of *anti*-7-benznorbornenol, m.p. 91–102°, infrared spectrum identical with pure material. Chromatography as above yielded 5.0 g., m.p. 104.1–105.7°, and subsequent fractions of lower melting point which could be purified by further chromatography but not by recrystallization alone; infrared spectrum of VII: 2.80, 3.00, *3.41*, 6.83, 6.88, 7.27, 7.77, 8.07, 8.42, 8.68, *9.00*, *9.33*, 9.87, 10.14, 10.76, 10.96, 11.48, 11.95, *13.38*.

Anal. Calcd. for $C\ H_2O$: C, 82.50; H, 7.50. Found: C, 82.71; H, 7.47.

***anti*-7-Benznorbornenyl *p*-bromobenzenesulfonate** melted at 132.5–135.0° after recrystallization.

Anal. Calcd. for $C_{17}H_{15}O_3SBr$: C, 53.83; H, 3.96. Found: C, 53.91; H, 4.11.

Treatment of the acetolysis product as described above for the *exo* isomer yielded an acetate with an infrared spectrum different from that of the *exo* product; reduction with lithium aluminum hydride in the same manner yielded a white crystalline product with an infrared spectrum identical with that of *anti*-7-benznorbornenol.

7-Benznorbornenone (VIII) was prepared by Oppenauer oxidation as described for 2-benznorbornenone. The principal carbonyl absorption in the infrared spectrum was at 5.58 μ; the ultraviolet spectrum in ethanol showed maxima at 211 mμ (log ε 3.8; the solvent *vs.* air had an absorption of 0.6 at this wave length, but the baseline of solvent *vs.* solvent remained at zero), at 257 (2.74), at 263 (2.92) and at 271 (2.95); infrared spectrum of **VIII**: 3.44, *5.55*, *5.58*, 5.70, 6.85, 7.12, 8.85, 8.95, 9.32, 9.43, 9.86, 11.30, 12.94, *13.43*, 1375, 14.35.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.54; H, 6.33. Found: C, 83.35; H, 6.45.

The 2,4-dinitrophenylhydrazone, from ethanol, melted at 143.6–146.4°. The ultraviolet spectrum showed maxima at 267 mμ (log ε 4.01) and at 358 (4.29).

Anal. Calcd. for $C_{17}H_{13}O_4N_4$: C, 60.35; H. 4.14. Found: C, 60.28; H, 4.38.

To 0.20 g. of 7-benznorbornenone in 20 ml. of ether was added lithium aluminum hydride in excess and the mixture was refluxed for four hours, then worked up in the usual manner. The product had an infrared spectrum identical with that of pure *anti*-7-benznorbornenol: recrystallized once from petroleum ether, m.p. 103.8–105.2°, mixed m.p. 103.8–106.2°.

***anti*-7-Benznorbornadienol (IX).**—To a mixture of several grams of *exo*-2-bromo *anti*-7-benznorbornenol in 22 g. of dihydropyran freshly distilled from potassium hydroxide was added a small drop of concd. sulfuric acid. A vigorous momentary reaction ensued; the reaction mixture turned dark and small amounts of black tar formed; the temperature rose above 40°. The remainder of 27.4 g. of bromohydrin was added and it all dissolved when the temperature remained above 30°. The sides of the flask were washed down with a small amount of ether and the mixture allowed to stand overnight. About 50 ml. of ether was added and the solution was shaken over sodium hydroxide pellets and left standing over sodium hydroxide for 3 hr. The cloudy solution was chromatographed over 300 ml. of Merck alumina in anhydrous ether. The combined residues from evaporation of the first four 500-ml. fractions were pumped

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[22] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 619.

[23] E. E. Royals and L. L. Harrell, Jr., THIS JOURNAL, **77**, 3405 (1955).

[24] H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957).

in a vacuum desiccator for several hr. This product was dissolved in benzene and heated with the potassium *t*-butoxide prepared under nitrogen from 5.0 g. of potassium metal.[25] After a total of 17 hours of heating at 80°, the dark brown benzene solution was decanted from the solid residue, which was refluxed for 0.5 hr. with more benzene and dissolved entirely in water. The combined benzene solution was washed 3 times with water and twice with saturated sodium chloride solution, then concentrated by evaporation. The residue was chromatographed over 300 ml. of Merck alumina in benzene. The residues of the first 1900 ml. of eluent were dissolved in 150 ml. of 95% ethanol, a solution of 15 ml. of 36% hydrochloric acid in 200 ml. of 95% ethanol added and heated to 75° on the steam-bath, then allowed to stand at room temperature overnight. Solid sodium carbonate was added until effervescence ceased; then the solution was filtered, evaporated under reduced pressure from a warm water-bath, and pumped with an oil-pump for 1 hr. after it was dry. The crude *anti*-7-benznorbornadienol was dissolved in 1 l. of boiling petroleum ether and chromatographed over 200 ml. of Davison activated silica gel, since alumina had been found to discolor this product. With 20% anhydrous ether in petroleum ether was eluted a total of 12.83 g. (71%) of white, crystalline product melting above 104°; recrystallized twice from petroleum ether, m.p. 106.3–108.2°; infrared spectrum of IX: 2.80, 3.24, 3.33, 6.87, *7.19*, 7.66, 8.00, *8.23*, *8.56*, 8.80, 9.03, *9.26*, *9.40*, 9.93, 10.81, 10.93, 11.57, 11.82, *12 34*, 12.58, 12.79, *13.51*, *14.29*.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.54; H, 6.33. Found: C, 83.57; H, 6.71.

***anti*-7-Benznorbornadienyl *p*-bromobenzenesulfonate**, m.p. 126.8–128.5°.

Anal. Calcd. for $C_{17}H_{13}O_3SBr$: C, 54.11; H, 3.45. Found: C, 54.54; H, 3.52.

***anti*-7-Benznorbornadienyl Acetate.**—To 0.20 g. of *anti*-benznorbornadienol in 1 ml. of pyridine was added 1 ml. of acetic anhydride and allowed to stand overnight, then pumped for 5 hr. with an oil-pump and allowed to stand overnight, in a vacuum desiccator over potassium hydroxide pellets. The residue was dissolved in ether, washed 3 times with cold dilute hydrochloric acid and twice with sodium carbonate solution and dried over anhydrous potassium carbonate. The residue after evaporation of the ether had an infrared spectrum identical with that of acetolysis product of *anti*-7-benznorbornadienyl brosylate.

When refluxed with lithium aluminum hydride in excess in ether overnight, this acetate yielded *anti*-7-benznorbornenol with an infrared spectrum identical with that of the authentic material described above and with that of the product of hydrogenation of *anti*-7-benznorbornadienol in ethanol over platinum catalyst. Reaction of *anti*-7-benznorbornadienyl acetate with methylmagnesium iodide regenerated *anti*-7-benznorbornadienol, identified by its infrared spectrum.

Oxidation of *anti*-7-Benznorbornadienol.—Oppenauer oxidation as described for 2-benznorbornenone yielded mostly naphthalene, identified by odor and by comparison of the infrared spectrum with that of an authentic sample; some unchanged *anti*-7-benznorbornadienol was recovered. Similar results were found using ether as solvent and refluxing for 5 days, and also using benzene as solvent and stirring for 9 days at room temperature. In the latter case the solvent was evaporated under reduced pressure and naphthalene was found in the Dry Ice trap after overnight pumping with an oil-pump.

Attempted Epimerization of *anti*-Benznorbornadienol.—When equimolar aluminum isopropoxide and *anti*-7-benznorbornadienol in about 3 ml. of xylene with a small amount of acetone according to the procedure of Doering and Aschner[26] was heated in a sealed tube at 100° for 5 days, most of the starting alcohol was recovered unchanged and a small amount of naphthalene was detected in the infrared spectrum. With sodium, fluorene and fluorenol by the procedure of Doering and Aschner[26] on similar heating at 100° for 5 days, the crude product showed no infrared absorption at 14.4 μ characteristic of the benznorbornadienyl double bond. Heating *anti*-7-benznorbornadienyl brosylate similarly with a tenfold excess of potassium acetate in acetone for 5 days at 100° produced a yellow varnish-like product which was eluted from Merck alumina only with 5% or more absolute ethanol in anhydrous ether. Refluxing a similar mixture in acetone for 40 hours brought about no reaction; after 7 days in a sealed tube at 76–78° mostly brosylate was recovered, but dissolving the residue in 3 ml. of petroleum ether and cooling to −25°, filtering, evaporating the mother liquor to half its volume and cooling and filtering again, the residue from the mother liquor showed strong peaks in the infrared spectrum at 2.70, at 5.90, and the peaks corresponding to the unsaturation were shifted to higher wave length than those in the spectrum of the brosylate. The 2,4-dinitrophenylhydrazone was red, showing maxima in its ultraviolet spectrum in ethanol at 263 mμ (log ϵ 4.40) and at 382 mμ (ϵ 4.50, calcd. for mol. wt. of 388), indicating a highly conjugated aldehyde.[27a]

The 2,4-dinitrophenylhydrazone of 1-naphthaldehyde[27b] prepared by the procedure of Brown and Subba Rao[28] showed maxima in its ultraviolet spectrum in ethanol at 310 mμ (log ϵ 3.3) and at 388 (3.9).

***exo*-Norborneol.**—Norbornylene was prepared from dicyclopentadiene and ethylene by the procedure of Thomas[29] and was hydrated by the procedure described above for *exo*-benznorborneol. The method of Bertram and Walbaum[19] was found to be far preferable: To 25 ml. of glacial acetic acid was added 4.9 g. of norbornylene and about 0.5 ml. of 50% sulfuric acid. The solution was heated under reflux for 1 hr. and it quickly turned dark gray. The reaction mixture was poured into 400 ml. of water, extracted twice with ether, and left overnight over solid sodium carbonate. The ether solution was washed twice with aqueous sodium carbonate solution and dried over magnesium sulfate. Charcoal was added and the solution filtered, then refluxed overnight in ether with excess lithium aluminum hydride.

When norbornylene oxide,[30] prepared as described above for benznorbornylene oxide, was left in refluxing ether with excess lithium aluminum hydride overnight and the ether all evaporated, working up in the usual manner yielded a mixture of *exo*-norborneol, identified by comparison of the infrared spectrum of the product with that of an authentic sample, and of 7-norborneol identified from the infrared spectrum of authentic material prepared by Norton.[31] When care was taken that the ether did not evaporate, after refluxing for 72 hr. the infrared spectrum of the product still showed some norbornylene oxide along with *exo*-norborneol; no 7-norborneol was detected.

exo-Norbornyl tosylate was prepared in the same manner as the brosylates described above; m.p. after several recrystallizations from petroleum ether, 53.0–54.5°.

Kinetic Procedures.—Acetolysis conditions and procedures were chosen to be similar to those of Norton and Woodward, which in turn had been chosen to be similar to those of Winstein, *et al.*,[32] and of Roberts, *et al.*[33] Samples of sulfonate ester were weighed into 50-ml. volumetric flasks so that solutions approximately 0.1 molar in ester would be obtained, then filled to 50 ml. with 0.100 molar sodium acetate from anhydrous sodium carbonate, glacial acetic acid, and refluxed for 5 hr. with sufficient acetic anhydride to leave 1% excess after removing the water of neutralization. Rate constants were determined by the infinity titer method, the first aliquot after thermal equilibrium had been reached was called zero time. Aliquots, usually 3 ml., were pipetted either from individual sealed ampoules which had been quenched in an ice-bath and then warmed to 25° or directly from the volumetric flask in the constant temperature bath and drained into 20 ml. of purified[34] dioxane. Two drops of a saturated solution of brom phenol blue in acetic acid was added, and the residual sodium acetate titrated with 0.020 molar perchloric acid in glacial

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[25] A. I. Vogel, "Practical Organic Chemistry," 3rd edition, Longmans, Green and Co., London, 1956, p. 920.

[26] W. von E. Doering and T. C. Aschner, THIS JOURNAL, **71**, 838 (1949).

[27] (a) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); (b) H. W. Coles and M. L. Dodds, THIS JOURNAL, **60**, 853 (1938).

[28] H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5379 (1958).

[29] C. L. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

[30] H. M. Walborsky and D. F. Loncrini, THIS JOURNAL, **76**, 5396 (1954); H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

[31] C. J. Norton, Ph.D. Thesis, Harvard University, 1955.

[32] S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, **70**, 812 (1948); S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[33] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

[34] L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., Boston, Mass., 1941, p. 369.

acetic acid which had been refluxed with 1% excess acetic anhydride. The disappearance of the yellow indicator color was taken as the end-point. Least squares slopes and their probable errors were calculated for plots of ln (% unreacted) against time; in all cases good straight lines were obtained for every run and at least one run for each compound was followed for three or more half-lives.

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CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Studies of Configuration. VIII. Evidence for Methoxyl Migration in the Solvolysis of 4-Methoxycyclohexyl Tosylate by Tritium Labeling[1]

BY DONALD S. NOYCE AND BRUCE N. BASTIAN

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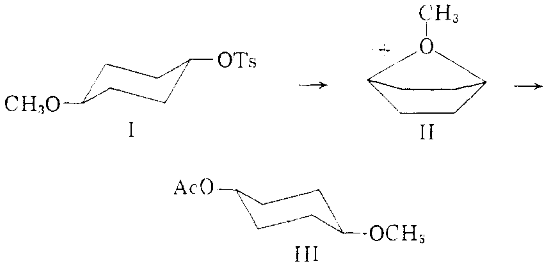
The preparation and solvolysis of *trans*-4-methoxycyclohexyl-1-*t* tosylate is reported. In acetic acid at 75° the solvolysis products are 66% 4-methoxycyclohexene, 9.6% *cis*-4-methoxycyclohexyl acetate and 24% *trans*-4-methoxycyclohexyl acetate. The tritium label is specifically in the 1-position in the olefin, demonstrating that none of the olefin arises from a symmetrical bicyclic oxonium ion intermediate II. The *cis*-4-methoxycyclohexyl acetate is likewise labeled only in the 1-position. The *trans*-4-methoxycyclohexyl acetate formed is nearly equally labeled in the 1- and 4-positions, demonstrating that it arises in large measure by an internally assisted pathway through the symmetrical ion II as an intermediate.

Introduction

In previous reports[2,3] from these laboratories we have demonstrated that the solvolysis of *trans*-4-methoxycyclohexyl tosylate (I) proceeds with some rate acceleration, and that the 4-methoxycyclohexyl acetate formed is largely of the *trans* configuration (III). It was concluded from the rate studies and the product studies that an internally assisted pathway was responsible for these results, with the symmetrical bicyclic oxonium ion (II) suggested as an intermediate. Winstein, Allred, Heck and Glick[4] have shown that the solvolysis of 4-methoxypentyl *p*-bromobenzenesulfonate proceeds through a similar intermediate.



It is the purpose of the present study to examine further the reality of II as an intermediate in the solvolysis of I. For this purpose it was decided to use *trans*-4-methoxycyclohexanol labeled in the 1-position with tritium (IV). Tritium labeling appeared to be particularly suitable. At the end of the sequence of reactions summarized in Chart I, reoxidation to 4-methoxycyclohexanone would provide a simple means of determining the partitioning of the solvolysis product to 4-methoxycyclohexanol-1-*t* and 4-methoxycyclohexanol-4-*t*. Furthermore the use of tritium in tracer quantities has a distinct advantage over the use of deuterium in molar concentrations. In the oxidation of a mixture of 1-*d*- and 4-*d*-labeled cyclohexanol the well-known isotope effect might well provide spurious results, if the cyclohexanol-1-*d* were not completely oxidized.

Results

With these considerations in mind, we examined the preparation of 4-methoxycyclohexanol-1-*t*. Sodium borohydride in isopropyl alcohol afforded a mixture of the *cis*- and *trans*-4-methoxycyclohexanol containing about 77% of the *trans* isomer. Reduction with tritium labeled sodium borohydride afforded a similar mixture. The mixture was diluted with a large amount of inactive *trans*-4-methoxycyclohexanol. Oxidation of this alcohol with chromic acid in acetone gave 4-methoxycyclohexanone, with 99.97% of the activity removed. This experiment serves to verify the specific labeling introduced.

trans-4-Methoxycyclohexanol-1-*t* (IV) was converted to the tosylate V, further diluted with inactive tosylate, and crystallized several times. Pure V ($2.62 \pm 0.05 \times 10^6$ d.p.m./mmole) was used for the solvolytic experiments. Solvolysis in acetic acid at 75° afforded a mixture of acetates ($2.71 \pm 0.05 \times 10^6$; VI, VII, VIII), and olefin ($2.33 \pm 0.3 \times 10^6$) which were separated by distillation. Both the olefin and the acetates were separately examined for the position of labeling.

A diluted aliquot of the olefin (0.13×10^6 d.p.m./mmole) was oxidized to β-methoxyadipic acid. After several crystallizations from hexane, the acid showed no activity. These results establish clearly that none of the olefin arises from the symmetrical intermediate.

The acetates from the solvolysis were saponified to yield a mixture of *cis*- and *trans*-4-methoxycyclohexanol ($2.62 \pm 0.02 \times 10^6$ d.p.m./mmole; IX, X, XI). Infrared analysis of this mixture showed that 71% was the *trans* isomer.

A sample of the mixed alcohols was oxidized with chromic acid in acetone to 4-methoxycyclohexanone. The specific activity of the ketone XII,

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[1] Supported in part by a grant from the National Science Foundation (NSF G-5921).

[2] D. S. Noyce and B. R. Thomas, THIS JOURNAL, **79**, 755 (1957).

[3] D. S. Noyce, B. R. Thomas and B. N. Bastian, *ibid.*, **82**, 885 (1960).

[4] S. Winstein, E. Allred, R. Heck and R. Glick, *Tetrahedron*, **3**, 1 (1958).