ACETOLYSIS OF A FUSED endo-NORBORNYL BROSYLATE

nmr spectral parameters and other physical data are also given. Recrystallized from ether-n-hexane, trans-2\beta-decalyl p-toluenesulfonate (1a-OTs) has mp 107-108°; nmr (CDCl₃) & 2.43, 7.55 (OTs), 4.80 (1 H, broad s, $W_{1/2} = 7$ Hz, C₆ eq H); ir (KBr) 909, 1174, 1342 cm⁻¹ (OTs); uv max (CH₃OH) 273.2 mµ (e 445).

Anal. Calcd for C17H24O8S1: C, 66.20; H, 7.85; S, 10.39. Found: C, 65.95; H, 7.79; S, 10.58.

Recrystallized from ether, 6-keto-trans-2β-decalyl p-toluenesulfonate (2a-OTs) has mp 102-103°; nmr (CDCl₃) § 2.45, 7.57 (OTs), 4.86 (1 H, broad s, $W_{1/2} = 7$ Hz, C₆ eq H); ir (KBr) 900, 1166, 1355 (OTs), 1715 cm⁻¹ (C=O); uv max (CH₃OH) 273.2 $m\mu$ (ϵ 456).

Anal. Calcd for C117H22O4S1: C, 63.33; H, 6.87; S, 9.94. Found: C, 63.07; H, 6.96; S, 9.84.

Recrystallized from acetone-n-hexane, 6-keto-∆⁵⁽¹⁰⁾-transdecalyl p-toluenesulfonate (3e-OTs) has mp 100-101.0°; nmr $(\text{CDCl}_{5}) \delta 2.46, 7.58 \text{ (OTs)}, 4.67 \text{ (1 H, broad s, } W_{1/2} \cong 23 \text{ Hz}, C_2 \text{ ax H}), 5.83 \text{ (1 H, broad s, } C_5 \text{ H}); \text{ ir (KBr) 1625, 1673 cm}^{-1}$ $(\alpha,\beta$ -unsaturated ketone).

Anal. Calcd for C17H20O4S1: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.45; H, 6.31; S. 9.90.

Recrystallized from acetone-*n*-pentane, $6-keto-\Delta^{5(10)}-cis-deca$ lyl *p*-toluenesulfonate (3a-OTs) has mp 121–122°; nmr (CD-Cl₃) δ 2.46, 7.60 (OTs) 4.93 (1 H, broad s, $W_{1/2} = 8$ Hz, C₂ eq H), 5.84 (1 H, t, J = 2 Hz, C₅H); ir (KBr) 1618, 1672 cm⁻¹ (α,β unsaturated ketone).

Anal. Calcd for C₁₇H₂₀O₄S₁: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.79; H, 6.34; S, 9.86. Kinetic Measurements.—The conditions and procedure for the

solvolyses in trifluoroacetic acid, acetic acid, and ethanol were the same as previously reported. $^{10}\,$

For formolysis, the tosylates were dissolved at a concentration of 20 mM in formic acid containing 22 mM sodium formate. The acid was purified by distillation with pure boric anhydride. Aliquots (1.0 ml) were distributed into tubes and sealed under nitrogen after freezing in Dry Ice-acetone. The tubes were placed in a constant-temperature bath and then successively withdrawn after appropriate intervals of time. The tubes were cooled and opened, and the contents were diluted with 10 ml of The solutions were titrated with 0.04 N perchloric acetic acid. acid in acetic acid using a Metrohm potentiograph E336A. Plots of log $(A_t - A_{\infty})$ vs. time, where \bar{A}_{∞} and \bar{A}_t are titers at infinity and at given times, respectively, were uniformly linear. The slopes multiplied by -2.303 gave the pseudo-first-order rate constants.

Acetolysis Products .- The method employed was essentially the same as that described previously.¹⁰ The olefin and acetate fractions were the separated by a small column of silica gel. The olefin fractions were collected, dried under reduced pressure, and weighed. The olefin fractions were shown to consist of the Δ^1 olefin and Δ^2 olefin by nmr and mass spectra and vpc analysis. The acetate fractions were collected and identified with authentic samples.¹⁴ The yields of the acetates were determined by vpc with internal standards. Products and yields from the tosylates (1-OTs-3-OTs) are given in the Results and, in part, in the preceding paper.¹⁰ The olefin fraction from **2a**-OTs showed nmr (CDCl₃) δ 5.5-5.7 (2 H, m, olefinic protons); mass spectrum m/e 150 (M⁺). That from **3e**-OTs showed nmr (CDCl₃) δ 5.75 (1 H, broad s, C₅ H), 6.2–6.3 (2 H, m, olefinic protons); mass spectrum m/e 148 (M⁺). That from **3a**-OTs showed nmr (CDCl₃) δ 5.75 (1 H, broad s, C₅ H), 6.2–6.3 (2 H, m, olefinic protons); mass spectrum m/e 148 (M⁺).

Registry No.—1a, 5746-69-0; 1a-OTs, 40429-90-1; 1e, 36667-73-9; 1e-OTs, 40429-92-3; 2a, 36667-84-2; 2a-OTs, 40429-94-5; 2e, 39089-10-6; 2e-OTs, 40429-96-7; 3a, 40429-97-8; 3a-OTs, 40429-98-9; 3e, 40429-99-0; 3e-OTs, 40550-47-8.

Formation of Endo Acetate in Acetolysis of a Fused endo-Norbornyl Brosylate via C-7 Participation^{1,2}

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XII-OH, a new alcohol, was obtained in low yield by sodium amalgam reduction of the oxymercurials from endo,endo diene. Upon acetolysis, XII-OBs undergoes ~98% rearrangement via cation A to VI-OBs; no endo acetate XIII-OAc is formed. Acetolysis of the endo brosylate XIII-OBs results in 22.5% XIII-OAc, apparently via C-7 participation and cation C.

In continuance of studies in the bird-cage hydrocarbon system,⁴ we reported⁵ recently that acetolysis of exo brosylate VI-OBs produced 27% endo acetate VII-OAc via anchimerically unassisted solvolysis in competition with anchimerically assisted solvolysis. The endo brosylate VII-OBs produced 3% VII-OAc through 10% intimate ion pair return to and subsequent solvolysis of VI-OBs.⁵ We now report the striking results of acetolysis of the related pair of brosylates XII-OBs and XIII-OBs, of which the most salient feature is formation of endo acetate XIII-OAc from endo brosylate XIII-OBs but not from exo brosylate XII-OBs.

(2) An extension of compound designations used previously⁴ is employed herein for ease of cross reference between the papers of this series (3) Deceased November 23, 1969.

Results and Discussion

XII-OH, a previously unknown alcohol,⁴⁻⁶ and thus XIII-OH became accessible as a result of studies⁷ of oxymercuration of endo.endo diene. Reaction of the diene^{7,8} with mercuric acetate in acetic acid, treatment of the reaction mixture with aqueous sodium chloride, and reduction of the resultant solid mixture with sodium amalgam in water led to formation of ca. 62% bird-cage hydrocarbon, 5% residual unhydrolyzed acetates, 24% VI-OH, a trace of V-OH, and 9%XII-OH (Scheme I). Isolation of 98% pure XII-OH containing 2% V-OH was effected by chromatography of the crude product mixture on alumina. Final purification by gas chromatography, sublimation,

⁽¹⁾ Taken in part from the Ph.D. Thesis of Robert K. Howe, UCLA, Los Angeles, Calif., 1965.

⁽⁴⁾ L. deVries and S. Winstein, J. Amer. Chem. Soc., 82, 5363 (1960).

⁽⁵⁾ Robert K. Howe, Peter Carter, and S. Winstein, J. Org. Chem., 37, 1473 (1972).

⁽⁶⁾ The alcohol with mp 72-73°, originally thought⁴ to possess the XII-OH

structure, has been shown⁵ to be the endo epimer of VI-OH. (7) K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

⁽⁸⁾ P. Bruck, D. Thompson, and S. Winstein, Chem. Ind. (London), 405 (1960).



and crystallization gave XII-OH, mp 84.5-85.0°, that contained < 0.05% of isomeric alcohols.

The structure of this new alcohol was deduced from the carbon and hydrogen analyses (consistent with $C_{12}H_{16}O$, from spectra of the alcohol and derived ketone, and from the XII-OBs acetolysis results. The ir spectrum of XII-OH distinguished this material from all the previously known C_{12} alcohols in our studies^{4,5,8-15} and revealed no CH absorption above 3000 cm^{-1} . Thus, XII-OH has no sterically opposed hydrogens¹¹ such as exist in IV-OH, V-OH, and XIV-OH. In the nmr spectrum of XII-OH, the α proton H_a appears as a very slightly broadened singlet at τ 6.25 (CCl₄ solvent), consistent with the assigned structure since the H_a -C-C- H_b dihedral angle is *ca*. $80-85^{\circ}$ and the H_a-C-C-H_c dihedral angle is ca. 70-75°, for which coupling constants of the order of 0-1Hz are to be expected.¹⁶ Similarly, half-cage V-OH exhibits a singlet (very slightly broadened) for the α proton.

XII ketone, derived from oxidation of XII-OH, has the carbonyl absorption at 1755 cm^{-1} , indicative of greater angle strain than in V ketone¹³ (1746 cm⁻¹), VI ketone⁵ (the ketone derived from VI-OH: 1746) cm^{-1}), and VIII ketone⁵ (1744 cm^{-1}). XII ketone exhibits no ir absorption at 1410-1420 cm⁻¹, which demonstrates the lack of a methylene group adjacent to the carbonyl group.¹⁷ Reduction of XII ketone with lithium aluminum hydride in ether proceeds with a high degree of steric approach control to yield 96.2% XIII-OH and 3.8% XII-OH. Pure

(9) S. Winstein and R. L. Hansen, Tetrahedron Lett., 4 (1960).
(10) S. Winstein and R. L. Hansen, J. Amer. Chem. Soc., 82, 6206 (1960). (11) D. Kivelson, S. Winstein, P. Bruck, and Robert L. Hansen, J. Amer.

- Chem. Soc., 83, 2938 (1961). (12) Peter Carter, Robert Howe, and S. Winstein, J. Amer. Chem. Soc., 87, 914 (1965).
- (13) R. Howe and S. Winstein, J. Amer. Chem. Soc., 87, 915 (1965).
- (14) S. Winstein, Peter Carter, F. A. L. Anet, and A. J. R. Bourn, J. Amer. Chem. Soc., 87, 5247 (1965).
 - (15) Peter Carter and S. Winstein, J. Amer. Chem. Soc., 94, 2171 (1972).
 - (16) M. Karplus, J. Chem. Phys., 30, 11 (1959).
 - (17) S. A. Francis, J. Chem. Phys., 19, 942 (1951).

XIII-OH, mp 177-177.5°, was obtained by fractional crystallization.

The most conclusive data for the structural assignment for XII-OH stems from the extensive rearrangement (ca. 98%) of XII-OBs to VI-OBs during acetolysis, a result reconcilable only with the structure proposed for XII-OH. The XII-OBs initial acetolysis rate constant, k_{XII} , drifts upward extremely rapidly; at 25°, $k_{XII} = 1.25 \times 10^{-6} \text{ sec}^{-1}$, and at 1% reaction (acid production) the integrated rate constant is 4.7 \times 10⁻⁶ sec⁻¹. The initial acetolysis rate constant, $k_{\rm XII}$, was determined fairly accurately by extrapolation to 0% reaction of a plot of integrated rate constant vs. per cent reaction. For this plot, titration points were taken as early as 0.102, 0.237, and 0.294%reaction. The acetolysis rate constant integrated from 76% reaction is quite steady at 4.03 \times 10⁻⁵ sec⁻¹, in good agreement with the value 3.91 \times 10⁻⁵ sec-1 reported⁴ for VI-OBs. The XII-OBs rearrangement rate constant, $k_r = 8.01 \times 10^{-5} \text{ sec}^{-1}$, was determined by the method of Young, Winstein, and Goering.¹⁸ The product mixture from solvolysis of 0.00663 M XII-OBs in acetic acid (0.020 M sodium acetate) at 50° was found to contain 64.8 \pm 1.5% VI-OAc, 27.9 \pm 1.5% VII-OAc, 6.5 \pm 0.5% twisted monoene (the $olefin^{4,5}$ derived from VI-OBs), 0.4% bird-cage hydrocarbon, 0.34% V-OAc, and 0.07% XII-OAc. There was less than 0.03% XIII-OAc (none detected). This product composition is identical within experimental error with that obtained from VI-OBs,⁵ except for the presence of ca. 1% of other products (birdcage hydrocarbon, V-OAc, and XII-OAc). Thus, both the kinetic analysis and the product mixture reveal the extensive rearrangement of XII-OBs to VI-OBs in acetolysis.

This rearrangement most likely occurs via an intimate ion pair consisting of cation A and brosylate anion. The ratio $k_r/k_{XII} = 64$ is a minimum measure of the ratio of ion pair return to VI-OBs and acid production from A in XII-OBs acetolysis, since part of $k_{\rm XII}$ is due to solvolysis via cation B (Scheme II).



⁽¹⁸⁾ W. G. Young, S. Winstein, and H. L. Goering, J. Amer. Chem. Soc., 73, 1958 (1951).

Since the intimate ion pair consisting of A and brosylate anion is the first intermediate formed in VI-OBs acetolysis, the ratio $k_r/k_{XII} = 64$ is also a minimum measure of ion pair return in VI-OBs acetolysis.⁵ The VI-OBs formed in XII-OBs acetolysis undergoes solvolysis via competing anchimerically assisted and anchimerically unassisted routes; the latter route results in formation of the VII-OAc observed in both XII-OBs and VI-OBs acetolyses.⁵ Formation of 1.7% of cation B from XII-OBs would account for the amounts of bird-cage hydrocarbon, V-OAc, and XII-OAc produced in XII-OBs acetolysis.¹⁹ Significantly, there is less than 0.03% (none detected) of the classical solvolysis product XIII-OAc produced.

XIII-OBs acetolyzed with fairly steady first-order kinetics, $k = (1.03 \pm 0.02) \times 10^{-5} \text{ sec}^{-1}$ at 50° and $k = (2.44 \pm 0.04) \times 10^{-4} \text{ sec}^{-1}$ at 75°, and produced 99% of the theoretical amount of acid. The titrimetric rate ratio $(k_r + k_{XII})/k_{XIII}$ is cd. 200 at 25°. Although the extent of ion pair return in XIII-OBs acetolysis is not known, it appears that XIII-OBs ionizes more slowly than XII-OBs. The product mixture from acetolysis of XIII-OBs at 50° was found to consist of 6.6% V-OAc, 49.9% VI-OAc, 6.1% VII-OAc, 1.9% VIII-OAc, 6.5% XII-OAc 22.5% XIII-OAc, 5.1% bird-cage hydrocarbon, and 1.4% twisted monoene. None of the other isomeric brosylates, including XII-OBs, yields any XIII-OAc. Anchimerically unassisted solvolysis of XIII-OBs would be expected to yield predominantly XII-OAc, and most of the 6.5% XII-OAc that is formed probably arises through this path. Even if a classical cation solvated on both sides were produced from XIII-OBs, more XII-OAc than XIII-OAc would be expected since the steric hindrance about the endo side of the carbonium ion is greater than that about the exo side.



(19) Acetolysis of X-OBS results in 100% cation B initially, which then

$$\begin{array}{c} BsO \\ \hline \\ X \cdot OBs \end{array} \rightarrow B \rightarrow \text{products}$$

forms 24% bird-cage hydrocarbon, 24% V-OAc, and 4.1% XII-OAc, among other products, after 100% acid production.⁵

(20) S. Winstein and D. Trifan, J. Amer. Chem. Soc., 74, 1154 (1952).

Apparently, the formation of 22.5% XIII-OAc from XIII-OBs can be rationalized only with anchimerically assisted ionization to form the nonclassical cation C (Scheme III); this is formed in competition with anchimerically unassisted ionization to give the classical cation. No detectable amount of XV-OAc was observed. Possibly part of the large amount of strain in this acetate is felt in the transition leading to it and makes its formation unfavorable.

For neighboring group participation to be effective, a trans coplanar arrangement of the participating group and the leaving group is generally required. For example, this requirement is met and participation occurs in solvolysis of *exo*-norbornyl brosylate.²⁰ The trans coplanar requirement is not met in *endo*-norbornyl brosylate, and this brosylate solvolyzes without C-7 participation. The XIII system is so twisted by the bond that joins the ethano bridges that the C₂-OBs bond and the C₁-C₇ bond are nearly trans coplanar. This allows C-7 participation^{21,22} to occur more readily than in the case of *endo*-norbornyl brosylate; there is at least 22.5% of cation C formed in XIII-OBs acetolysis.

The 5.1% bird-cage hydrocarbon, 6.6% half-cage V-OAc, and 1.9% VIII-OAc arise via cation B, which is formed from C and/or the XIII-OBs classical cation. The remainder of the product mixture arises via cation A. Since the cation A and the brosylate anion are generated from XIII-OBs with a geometry relatively unfavorable for ion-pair return, ca. 71% of the A cations produced undergo collapse with solvent to give VI-OAc and only ca. 29% undergo ion pair return to VI-OBs, which then forms the observed amounts of VII-OAc and twisted monoene.

Experimental Section

Melting points are corrected. Standard acetolysis procedures were employed ${}^{\scriptscriptstyle 28}$

1,4,4a,5,8,8a-Hexahydro-endo,endo-1,4:5,8-dimethanonaphthalene (Endo,endo Diene).²⁴—Caution. Unpleasant physiological reactions (headache, depression) upon exposure to this diene have been experienced by two workers. Avoid inhalation of the vapors of and skin contact with this material. To 50 g (0.137 mol) of technical grade isodrin and 93 g (1.26 mol) of tert-butyl alcohol in 400 ml of dry THF stirred under nitrogen in a 5-1. flask fitted with an efficient reflux condenser and stirrer was added 17.5 g (2.52 mol) of lithium wire cut into 0.5-in. lengths so as to allow the freshly cut pieces to fall directly into the flask. The mixture was stirred vigorously under nitrogen. An exothermic reaction ensued with considerable foaming, and the solvent began to boil violently. Ice-bath cooling was employed only as long as necessary to keep the reaction under control. The reaction was

⁽²¹⁾ Solvolysis of 1-methoxy-2-endo-norbornyl brosylate provided the first example of C-7 participation and ring contraction (5-9%) in solvolysis of a norbornyl system: Y.-i Lin and A. Nickon, J. Amer. Chem. Soc., **92**, 3496 (1970). Formation of the rearranged oxocarbonium ion in this system provides a measure of stabilization and driving force not present in the parent norbornyl system.

⁽²²⁾ Several examples of C-7 migration from C-1 to C-2 exist in vibrationally excited ("hot") carbonium ions generated from certain substituted endo-norbornyl diazonium ions: C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, J. Amer. Chem. Soc., **89**, 3940 (1967); P. Yates and R. J. Crawford, *ibid.*, **88**, 1561 (1966); W. Kirmse, G. Arend, and R. Siegfried, Angew. Chem., Int. Ed. Engl., **9**, 165 (1970); W. Kirmse and G. Arend, Chem. Ber., **105**, 2738, 2746 (1972).

⁽²³⁾ S. Winstein, C. Hansen, and E. Grunwald, J. Amer. Chem. Soc., 70, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70, 821 (1948).

⁽²⁴⁾ Since the diene is unstable in air (half-cage V ketone is formed in good yield within a few hours), no delays in the preparation should be allowed until after formation of the silver nitrate complex.

stirred until the spontaneous reflux subsided (0.75 to 1.5 hr) and then was held at reflux on a steam bath for 0.5 hr. The hot mixture was poured through a wire screen to remove residual pieces of lithium. Crushed ice and then 11. of water were added, and the mixture was extracted three times with pentane. The pentane extracts were combined, washed with water, dried (Na₂SO₄), and distilled. From two such runs a total of 36.7 g (85% yield)of crude diene, bp 62-80° (2 mm), was obtained.

A 22-g sample of crude diene was added to a solution of 67 g of silver nitrate in 54 ml of water with stirring under nitrogen. To the resultant solid cake was added 216 ml of absolute ethanol, and the mixture was stirred with a stirring rod. The mixture was then stirred under nitrogen overnight. The white precipitate was collected and washed with ethanol. Upon exposure to air, the 39.5 g of diene-silver nitrate complex, mp 207° dec, turned gray. It was stored under nitrogen in a tightly sealed bottle at -10° in a freezer.²⁵

A mixture of 39.5 g of complex and 11. of concentrated ammonium hydroxide in a 3-1. flask fitted with a spiral condenser was heated on a steam bath. Periodically, the solid diene which steam distilled into the condenser was washed out with pentane, and additional ammonium hydroxide was added to the flask. This process was repeated until diene no longer formed in the condenser (2-3 hr or longer). The aqueous mixture was cooled and extracted with pentane. All the pentane washings and extracts were combined, washed with water, dried (Na₂SO₄), and concentrated. The residual white solid was sublimed at 80° (1 mm) to give 9.0 g (41% from the crude diene) of solid, mp 94–96° (lit.⁷ mp 90-92), that was 99.3% endo, endo diene and 0.7%endo,endo monoene (gc analysis on a 25% SE-30 on Chromosorb W colunn²⁶): ir (CCl₄) 3.21 (w), 3.30 (m), 3.41 (s), 3.52 (m), 6.39 (w), 6.90 (m), 7.49 (s), 7.88 (w), 8.00 (s), 8.11 (w), 8.20 (w), 8.85 (m), 9.12, (w), 9.71 (w), 10.13 (w), 10.35 (w), 10.99 (s), 11.31 (s), 11.45 (s), 14.00 (vs), 14.50 μ (w).

Decahydro-4,7-methano-2,5,8-methenoazulen-exo-3-ol (XII-OH) -To a solution of 9.0 g (0.0570 mol) of endo, endo diene in 200 ml of acetic acid was slowly added in small portions 18.1 g (0.0568 mol) of mercuric acetate. After a few minutes the pale yellow solution was filtered into 600 ml of aqueous NaCl solution. The white precipitate was collected after 1 day, washed with water and pentane, and shaken for 13 hr with 350 g of 3% sodium amalgam in 250 ml of water. The cloudy mixture was extracted with three 100-ml portions of ether. The ether extracts were combined, dried (Na_2SO_4), and concentrated to a colorless oil. Gc analysis indicated the oil to consist of 62% bird-cage hydrocarbon, 24% VI-OH, 9% XII-OH, a trace of V-OH, and 5% acetates. The oil was chromatographed on a 1.25×14 in. column of neutral, activity 2.5 alumina. Bird-cage hydrocarbon, 3.5 g, was eluted with pentane. Elution with 10% ether in pentane yielded 0.46 g of acetate mixture. Elution with 20% ether in pentane gave first 0.67 g of XII-OH, mp 81-83°, then 0.30 g of a 40:60 mixture of XII-OH and VI-OH, and finally 1.85 g of VI-OH. Two crystallizations of the VI-OH from pentane at 5° gave 1.1 g of VI-OH, mp 75.5-76.5° (lit.¹ mp 76.2-77.6°). The XII-OH was crystallized five times from pentane to give

0.23 g of XII-OH, mp 85.5–86.5°, that contained ca. 2% of V-OH (gc assay).

Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.22.

The XII-OH was further purified by gas chromatography on a UCON 50-HB 2000 column, sublimation, and crystallization from pentane at -20° to give XII-OH, mp 84.5-85.0°, that contained less than 0.05% of isomeric alcohols (gc assay).

XII-OBs.—A solution of 75 mg of pure XII-OH and 218 mg of brosyl chloride (100% excess) in 2 ml of pyridine was held at 0° for 26 hr. Ice water, 30 ml, was added, and the mixture was extracted with three 15-ml portions of ether. The combined ether extracts were washed with three 25-ml portions of 2 N HCl, three 25-ml portions of saturated NaHCO₈ solution, and 50 ml of water. The ether solution was dried (Na_2SO_4) and concentrated under vacuum at 20° to an oil. The oil was dissolved in 25 ml of pentane at 20°. The solution was concentrated with a stream of nitrogen; when crystallization began, the mixture was placed in a freezer. The resultant solid XII-OBs was recrystallized in the same way to give 75 mg of XII-OBs, mp 80-81.5°, which produced 98% of the theoretical amount of acid upon acetolysis.

Anal. Calcd for C₁₈H₁₉SO₃Br: C, 54.68; H, 4.84. Found: C, 54.88; H, 4.92.

Decahydro-4,7-methano-2,5.8-methenoazulen-3-one (XII Ketone).-Solutions of 150 mg of 98% pure XII-OH in 10 ml of ether and 2.0 g of CrO_8 in 10 ml of water were stirred together for 4 hr. Then 50 ml of pentane was added, and the organic layer was washed with water until it was colorless. The solvent was removed under vacuum, and the ketone was chromatographed on alumina and sublimed at 90° (0.5 mm) to give 90 mg of XII ketone, mp 146.5–148.5°, that was 99% pure (gc assay; ca. 1%V ketone was present): ir (CCl₄) 1755 ± 1 cm⁻¹ (C=O).

Anal. Caled for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C, 82.68; H, 8.28.

Decahydro-4,7-methano-2,5,8-methenoazulen-endo-3-ol (XIII-OH).-Reduction of 10 mg of 99% pure XII-OH with excess lithium aluminum hydride in ether gave an alcohol mixture that contained 96.2% XIII-OH, 3.8% XII-OH, and a trace of halfcage oxygen-inside alcohol (gc assays on NMPN and UCON columns). On a larger scale, 0.56 g of XII-OH that contained 1% V-OH and 4% VI-OH was oxidized, and the resultant crude XII ketone was reduced with excess lithium aluminum hydride. The crude alcohol mixture was crystallized twice from pentane at pure (gc assay) XIII-OH, mp 177-177.5°, as fine needles. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.86, H, 9.35. -10° and five times from aqueous ethanol to give 0.15 g of 100%

XIII-OBs.-From 70 mg of XIII-OH and 218 mg of brosyl chloride there was obtained (by the method employed for XII-OBs) 90 mg of XIII-OBs, mp 107.5-108.5°, which produced 99% of the theoretical amount of acid upon acetolysis.

Anal. Calcd for C18H19SO3Br: C, 54.68; H, 4.84, Found: C, 54.87; H, 4.70.

XII-OBs Acetolysis Products.—A 25-ml solution (0.0066 M XII-OBs) was prepared from 65.5 mg of XII-OBs and acetic acid that contained 0.020 M sodium acetate. The solution was held at 50° for 4.16 hr (20 half-lives of VI-OBs), cooled, and diluted with 25 ml of pentane. The solution was extracted with 50 ml of The water layer was extracted with 15 ml of pentane. water. The pentane layers were combined, extracted with three 25-ml portions of saturated NaHCO₃ solution and 50 ml of water, dried (Na₂SO₄), and concentrated to 1 ml with use of a 0.375×14 in. column packed with glass helices. Gc analysis on a 0.25 in. \times 4 m column of 5% DOW X2405 on Chromosorb W, 80–100 mesh, at 155° and 30 psi helium pressure, indicated the product mixture to consist of $65.2 \pm 1.5\%$ V-OAc plus VI-OAc plus XII-OAc (retention time 67 min), $27.9 \pm 1.5\%$ VII-OAc (retention time 57 min), $6.5 \pm 0.5\%$ twisted monoene (retention time 5.5 min), and 0.4% bird-cage hydrocarbon (retention time 5.1 min). acetates were converted to alcohols with excess lithium aluminum hydride. Gc analysis on a UCON 50-HB 2000 column showed the alcohol fraction to consist of 99.56% VI-OH plus VII-OH, 0.07% XII-OH, and 0.37% V-OH. There was <0.03% XIII-OH (none detected).

XIII-OBs Acetolysis Products.—A 16-ml solution (0.00984 MXIII-OBs) was prepared from 62.2 mg of XIII-OBs and acetic acid that contained 0.02 M sodium acetate. The solution was held at 50° for 328.5 hr (17.5 helf-lives). After work-up, the product mixture was analyzed on the DOW X2405 column and was found to consist of 5.1% bird-cage hydrocarbon, 1.4% twisted monoene, 8.0% VII-OAc plus VIII-OAc, and 85.5%V-OAc plus VI-OAc plus XII-OAc plus XIII-OAc.

The acetates were converted to alcohols with excess lithium Ge analysis on a 0.125 in. \times 5 ft aluminum hydroxide in ether. column of 5% UCON 50-HB 2000 on Chromosorb W, 80-100 mesh, at 150° revealed the alcohol fraction to consist of 61.8% VI-OH plus VII-OH plus VIII-OH (unresolved, retention time 16.6 min), 24.1% XIII-OH (retention time 19.8 min), 7.0% XII-OH (retention time 21.1 min), and 7.1% V-OH (retention time 23.9 min).

⁽²⁵⁾ The silver nitrate complex has been stored at -10° for 6 months with no apparent decomposition or impairment of the purity of the diene

⁽²⁶⁾ Traces of acid in the gc system, including acid-washed column supports, cause rearrangement of the diene to bird-cage hydrocarbon and twisted monoene and should be avoided.

The alcohol mixture was oxidized to a ketone mixture, which then was analyzed by gc on a 0.125 in. imes 20 ft column of 2% UCON 50-HB 2000 on Chromosorb W, 80-100 mesh, at 150°. Less than 0.1% of any of the alcohols remained unoxidized. The ketone mixture consisted of 7.23% V ketone (retention time 35.5 min), 33.1% VIII ketone plus XII ketone (unresolved, retention time 37.7 min), and 59.7% VI ketone (retention time 42.1

min). Since the alcohol mixture consisted of 31.1% XII-OH plus XIII-OH, there must have been 2.0% VIII ketone in the ketone mixture and thus 2.0% VIII-OH in the alcohol mixture.

Combination of the data from the three gc analyses gave the composition of the XIII-OBs acetolysis product mixture: 6.6% V-OAc, 49.9% VI-OAc, 6.1% VII-OAc, 1.9% VIII-OAc, 6.5%

XII-OAc, 22.5% XIII-OAc, 5.1% bird-cage hydrocarbon, and 1.4% twisted monoene.

Registry No.—VI-OH, 40577-16-0; XII-OH, 40577-17-1; XII-OBs, 40577-18-2; XII ketone, 40577-19-3; XIII-OH, 40577-20-6; XIII-OBs, 40577-21-7; endo,endo diene 1076-13-7; brosyl chloride, 98-58-8.

Isobutyraldehyde. The Kinetics of Acid- and Base-Catalyzed Equilibrations in Water¹

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The rates and equilibrium constants for the reversible acid- and base-catalyzed hydration of isobutyraldehyde in water have been determined by temperature jump and nmr spectrometry. The standard enthalpy and entropy changes for isobutyraldehyde hydration are -5.6 kcal/mol and -19.9 eu. The standard enthalpy and entropy for the reaction of isobutyraldehyde hydrate with hydroxide ion is 0.6 kcal/mol and -1.9 eu. The activation enthalpies for the hydrogen ion and hydroxide ion catalyzed hydration of isobutyraldehyde are 7.8 and 11.7 kcal/mol, respectively.

Among the many studies on the hydration of aldehydes and ketones² are reports concerning isobutyraldehyde.³⁻⁷ A solution of isobutyraldehyde in water equilibrates rapidly to a mixture of hydrate (h), hydrate anion (h_) and isobutyraldehyde (a) (Scheme I).



$$K_{h} = \frac{1}{[a]}$$
(1)

$$K_{h} = \frac{[h_{-}]}{[h_{-}][OH^{-}]}$$
(2)

$$K_{ao^{-}} = \frac{[h_{-}]}{[a][OH^{-}]}$$
(3)

In connection with various studies on isobutyraldehyde we needed reliable values of these rate and equilibrium constants over a wide range of temperatures. Recently Pocker and Dickerson reported on the rates

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of hydration of isobutyraldehyde.^{8b} By extrapolation to a time immediately following the mixing of reactants, and assuming the extinction coefficient of the free aldehyde to be temperature independent, they were able to obtain values of K_h at several temperatures. A plot of log K_h vs. 1/T gave values of K_h at 25 and 35° in good agreement with the earlier values^{4b} obtained by nmr experiments. However, the nmr data were not corrected for possible saturation effects, and the hydration above 25° is so fast as to make extrapolation to zero time much less reliable than at 0°. Furthermore, a precise relationship between In K_h and reciprocal temperature, especially around 25–35°, is necessary for a study by temperature jump spectrometry. A rapid kinetic technique was necessary to study hydroxide ion catalysis under conditions where the hydroxide ion concentration was known accurately.

Experimental Section

Isobutyraldehyde (bp $63.5-64.0^{\circ}$) was freshly distilled before preparing solutions. No impurities were detected by glpc analysis. Oxidation of isobutyraldehyde to isobutyric acid was negligible under the conditions used. Doubly distilled dust-free degassed water (boiled) was used for the preparation of all solutions. Standard solutions of perchloric acid and sodium hydroxide were periodically checked by use of primary standard (potassium hydrogen phthalate) by titration to a phenolphthalein end point. Carbonate-free sodium hydroxide solutions were prepared by filtration of saturated sodium hydroxide solutions.

T-Jump and combined T-jump stopped-flow experiments were conducted on a Durrum-Gibbson stopped-flow spectrometer equipped with a D-150 modular control unit. A permanent record of the photomultiplier signal was obtained by photographing the image on a Tektronix 564 storage oscilloscope.

A standard solution of about $0.08 \ M$ isobutyraldehyde was placed in one of two storage reservoirs. Acid catalysis was studied by placing $0.02-0.18 \ M$ perchloric acid in the second reservoir. The ionic strength of the acid solution was adjusted to 0.2 by adding sodium chloride. Equal volumes of the two solutions were mixed by actuating the stopped-flow apparatus, and T-jump experiments were conducted on the resultant mixture (ionic strength 0.1). The effect of base on the rate of equilibration was studied by placing in the second reservoir solutions 0.02-0.1 M in sodium hydroxide with enough sodium c'hloride to give an ionic strength of 0.2. Since isobutyraldehyde and base react to form aldol condensation products, it was neces-