Competition between Anchimerically Assisted and Anchimerically Unassisted Routes in Solvolyses of Fused Norbornyl Derivatives[1,2]

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Received July 22, 1971

The products of acetolysis at 50° of VI-OBs are 65.3% VI-OAc, 27.3% VII-OAc, and 7.4% twisted monoene. VII-OBs produces 96.3% VI-OAc, 3.1% VII-OAc, and 0.6% twisted monoene. VIII-OBs produces 90.7% VIII-OAc, 2.6% IX-OAc, 6.7% twisted monoene, and 0.006% V-OAc. IX-OBs produces 99.22% VIII-OAc, 0.25% IX-OAc, and 0.53% twisted monoene. The very reactive X-OBs ($k = 0.104$ sec^{-1} at 27°) forms 14.5% bird-cage hydrocarbon, 0.06% twisted monoene, 25.3% V-OBs, 15.0% V-OAc, 14% VI-OBs, 19% VI-OAc, 5.4% VIII-OBs, 3% VIII-OAc, and 3.8% XII-OAc in acetic acid at 27°. The results suggest that endo acetates VII-OAc and IX-OAc produced in acetolysis of VI-OBs and VIII-OBs, respectively, are formed by anchimerically unassisted solvolysis in competition with anchimerically assisted solvolysis. The olefin appears to arise from concerted (probably cis) elimination from covalent VI-OBs and VIII-OBs. Formation of olefin and endo acetate in acetolysis of VII-OBs and of IX-OBs evidently results, in each case, from the small amount of exo brosylate produced from the endo brosylate *via* ion pair return.

In continuance of studies[4] of the solvolysis of the *p*-bromobenzenesulfonates VI-OBs and VIII-OBs, we have found that endo products are formed from these exo brosylates and also from the endo brosylates VII-OBs and IX-OBs. The present work provides further examples[5] of the competition between anchimerically assisted and anchimerically unassisted routes in solvolyses of norbornyl derivatives and provides insight into the mechanism of olefin formation from norbornyl brosylates.

Results

VI-OH, VI-OBs, VIII-OH, and VIII-OBs were known previously.[4] The structure of the previously reported[4] alcohol of mp 71.5–72.6° has been revised to that of VII-OH indicated below. Oxidation of both VI-OH and VII-OH gave the same ketone (VI-ketone), and lithium aluminum hydride reduction of VI-ketone gave a 31:69 mixture of VI-OH and VII-OH. Oxida-

VI-OH   VI-ketone

VII-OH
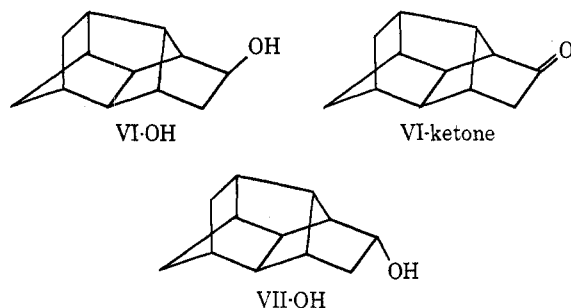
tion of VIII-OH and lithium aluminum hydride reduction of the resultant VIII-ketone gave a 9:91 mixture of VIII-OH and IX-OH, from which pure IX-OH was isolated.

(1) An extension of the compound designations used previously[4] is employed herein for ease of cross reference between past, present, and future papers in this series.

(2) Taken in part from the Ph.D. thesis of Robert K. Howe, UCLA, March 1965.

(3) Deceased Nov. 23, 1969.

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

(5) Other recent examples: (a) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969); (b) H. Tanida, T. Irie, and T. Tsushima, *ibid.*, **92**, 3404 (1970); (c) R. Muneyuki and T. Yano, *ibid.*, **92**, 746 (1970); (d) G. W. Oxer and D. Wege, *Tetrahedron Lett.*, 457 (1971).

The brosylates were solvolyzed at 50° at 0.010 *M* concentration in acetic acid that contained 0.020 *M* sodium acetate for 20 half-lives for the product analyses, which were performed by gas chromatography (gc). The product mixture from VI-OBs was found to consist of 65.3 ± 1.5% VI-OAc, 27.3 ± 1.5% VII-OAc, and 7.4 ± 0.5% twisted monoene,[4] with <0.03% XII-OAc (none detected). This analysis by gc is in agreement with the infrared analysis reported previously,[4] taking into consideration the corrected structural assignment for VII-OH and VII-OAc. VII-OBs gave 96.3% VI-OAc, 3.1 ± 0.3% VII-OAc, and 0.6 ± 0.2% twisted monoene, with <0.03% XII-OAc; acetolysis of VII-OBs under similar conditions but with incorporation of 0.02 *M* tetrabutylammonium *p*-bromobenzenesulfonate gave the same product mixture. Pure VIII-OBs yielded 90.7% VIII-OAc, 2.6% IX-OAc, 6.7% twisted monoene, and 0.006% half-cage V-OAc. Pure IX-OBs produced 99.22% VIII-OAc, 0.25 ± 0.10% IX-OAc, and 0.53% twisted monoene.

The acetolysis rate data are summarized in Table I.

TABLE I
FIRST-ORDER RATE CONSTANTS, ACETOLYSIS AT 25°

ROBs	$10^6 k$, sec^{-1}
VI-OBs[a]	39.1
VII-OBs[a]	57.0
VIII-OBs[a]	8.54
IX-OBs	2.30

[a] Reference 4.

Our previous attempts to prepare X-OBs had resulted in isolation of V-OBs, identified by melting point, elemental analysis, and first-order acetolysis rate constant.[6] In the present work the extremely reactive X-OBs was prepared by a low-temperature method. This brosylate produces 14.5% bird-cage hydrocarbon,[4] 0.06% twisted monoene, 25.3% V-OBs, 15.0% V-OAc, 14% VI-OBs, 19% VI-OAc, 5.4% VIII-OBs, 3% VIII-OAc, and 3.8% XII-OAc in acetic acid at 27° with a first-order rate constant of 0.104 sec^{-1}.

(6) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 590 (1960).

SCHEME I

Discussion

Several years ago[7,8] we had discussed the competition between k_Δ (anchimerically assisted) and k_s (anchimerically unassisted) routes in ionization of *exo*-norbornyl brosylate. Anchimerically assisted ionization predominates with the exo brosylate, and the products arise very predominantly *via* the nonclassical ion.[7,8] In 75% aqueous acetone, the resultant alcohol is >99.98% exo.[8] We discussed[8,9] solvolysis of *endo*-norbornyl brosylate on the basis of anchimerically unassisted ionization (with, however, any nucleophilic solvent assistance that may be present[10]) to a classical carbonium ion species. A major fraction of the classical ions underwent leakage to the nonclassical ions, while the remaining fraction collapsed directly to inverted *exo* product (7% in acetic acid). If the stability of the norbornyl nonclassical ion could be lowered sufficiently so as to approach that of the classical ion, then solvolysis of the exo brosylate could produce detectable proportions of endo products. Such is the case in the work presented here.[5]

The acetolysis titrimetric rate ratio at 25° of VI-OBs and VII-OBs is 0.69:1. This rate ratio indicates either that the nonclassical and classical ions in this system are of comparable energy or that the nonclassical ion is not involved in VI-OBs acetolysis. The titrimetric rate constant, k_t, of VI-OBs acetolysis appears to be considerably smaller, however, than k_Δ, the rate constant for anchimerically assisted ionization, for there appears to be very pronounced ion pair return in VI-OBs acetolysis. XII-OBs has been found[2,11] to rearrange *ca.* 98% to VI-OBs through the same ion pair produced in VI-OBs acetolysis. The ratio of the rearrangement rate constant to the solvolysis rate constant of XII-OBs is greater than 64:1. This provides

a rough measure for the partitioning of the carbonium ion from VI-OBs between ion pair return and collapse to product. The k_Δ for VI-OBs acetolysis thus may be 65 times greater than the titrimetric rate constant; this would indicate the exo/endo ionization rate ratio to be of the order of 45:1. The *ca.* 65% retention of configuration, in contrast to predominant inversion in classical solvolysis of secondary substrates,[12] and the exo/endo ionization rate ratio suggest that VI-OBs acetolysis involves a nonclassical ion. The rate constant for formation of VI-OAc *via* the anchimerically assisted pathway is the product of k_Δ and F, where $F = 1/65$, the fraction of nonclassical ion pairs that produces VI-OAc. Since $k_\Delta F$ is of the magnitude of the rate constant k_s (estimated from the VII-OBs rate) expected for anchimerically unassisted solvolysis, product formation occurs quite significantly from both the anchimerically assisted and anchimerically unassisted routes of solvolysis. The k_s route results in predominant inversion[12] and produces 27.3% endo acetate in VI-OBs acetolysis *via* the classical carbonium ion (Scheme I). Attack on the VI-OBs nonclassical cation to form XII-OAc is not observed. Evidently, the greater strain in the XII system[2,11] is manifested in the transition state leading to it and also, to a lesser degree, in the VI-OBs nonclassical ion. This strain results in less stabilization than usual for a norbornyl nonclassical ion.

Acetolysis of half-cage V-OBs results in ion pair return to VIII-OBs *via* the VIII-OBs nonclassical ion.[4] Thus, ion pair return in VIII-OBs acetolysis must make the titrimetic rate constant a low measure of k_Δ for VIII-OBs. The available data do not permit an estimate of the extent of ion pair return in this case. In VIII-OBs acetolysis, as in VI-OBs acetolysis, classical solvolysis with inversion[12] *via* the classical carbonium ion (Scheme II) is competitive with product formation from the nonclassical ion; 2.6% endo product is produced by the classical path. Only *ca.* 0.006% V-OAc is formed in VIII-OBs acetolysis. There is severe non-

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

(8) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(9) S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

(10) Our previously stated thought [S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951)] that solvolysis of certain secondary aliphatic systems "may approach the *Lim.* category in acetic acid and more closely in formic acid" implies some residual nucleophilic solvent assistance to ionization in acetic acid. The extent of residual solvent assistance, of course, can vary considerably with the secondary substrate.

(11) Robert K. Howe and S. Winstein, to be published.

(12) (a) A. Streitwieser and T. D. Walsh, *Tetrahedron Lett.*, 27 (1963); (b) M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966); (c) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968).

SCHEME II

bonded repulsion between the opposed transannular hydrogen atoms of V-OAc.[13]

The large selectivity of attack by solvent on the VIII-OBs nonclassical cation is a result of some of this strain being present in the transition state leading to V-OAc.

Acetolysis of the extremely reactive X-OBs has revealed the nature of olefin formation from VI-OBs and VIII-OBs. X-OBs acetolyzed at 27° to a first infinity of 53.5% acid production with a first-order rate constant of 0.104 sec⁻¹. Analysis at this stage of acetolysis revealed the product mixture to contain 0.06% twisted monoene, 14% VI-OBs, 19% VI-OAc, 5.4% VIII-OBs, and 3% VIII-OAc, among other products. The 0.06% twisted monoene is a maximum value; some or all of this could have arisen from VI-OBs or VIII-OBs in the alumina chromatography used to isolate the hydrocarbon products. The carbonium ion that forms VI-OAc therefore produces at most 0.3% twisted monoene. Since VI-OBs acetolysis produces 7.4% twisted monoene, at least 96% of the elimination from VI-OBs appears to be concerted and not from the fully developed carbonium ion. Similarly, the elimination from VIII-OBs probably arises largely, if not completely, by concerted elimination from covalent brosylate. The concerted elimination most likely is cis.[14]

The ratio of twisted olefin to VII-OAc is the same (within experimental error) in acetolysis of VI-OBs and VII-OBs. This may be fortuitous; however, it is also consistent with formation of *ca.* 10% VI-OBs in VII-

(13) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, **83**, 2938 (1961).

(14) In pyridine at 100°, IV-OBs[4] forms 75% endo-exo monoene, and IV-D-OBs forms 55% monoene with a k_H/k_D isotope effect of 2.85 for elimination (97.5% cis) and 1.10 for ionization; III-OBs,[4] the corresponding endo brosylate, forms less than 1% monoene directly. In acetic acid at 100°, IV-D-OBs produces 0.95% monoene with a k_H/k_D isotope effect of 2.8,

IV-OBs, X = H
IV-D-OBs, X = D
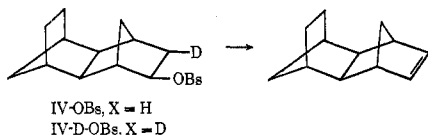
consistent with a concerted cis elimination in this solvent (P. Carter, unpublished results).

OBs acetolysis. This amount of VI-OBs would produce *ca.* 3% VII-OAc and *ca.* 0.7% twisted monoene, as is observed. This interpretation would indicate that there is very little direct elimination from VII-OBs.[14]

Information on the mechanism of formation of VI-OBs in VII-OBs acetolysis was sought by means of an acetolysis experiment with added brosylate anion. In the acetolysis of 0.010 M VII-OBs in the presence of 0.02 M sodium acetate, the average concentration of sodium brosylate, produced by neutralization of the liberated brosylic acid by the sodium acetate, is 0.005 M. The addition of 0.02 M tetrabutylammonium brosylate would result in an average brosylate salt concentration of 0.025 M, five times that without added brosylate salt. If VI-OBs were formed in VII-OBs acetolysis by brosylate anion attack on covalent VII-OBs or on a VII-OBs ion pair, five times the 3.1% VII-OAc would be expected. In fact, addition of 0.02 M tetrabutylammonium brosylate was shown to have no effect on the amount of VII-OAc produced in VII-OBs acetolysis.

Another pathway for formation of VI-OBs from VII-OBs exists. This involves rearrangement within intimate ion pairs as illustrated in Scheme I.[15] Similarly, formation of 7% VIII-OBs from IX-OBs *via* the illustrated path (Scheme II) would result in formation of 0.5% twisted monoene and 0.2% IX-OAc in IX-OBs

(15) Such endo-OBs to exo-OBs isomerization through intimate ion pairs has been observed directly by nmr and kinetic measurements in the partial isomerization of endo V-N-OBs in acetic acid to the much less reactive exo V-OBs. In this case, 24% of V-OBs is formed from V-N-OBs at 25° (R. Howe and P. Carter, unpublished results).

V-N-OBs   V-OBs
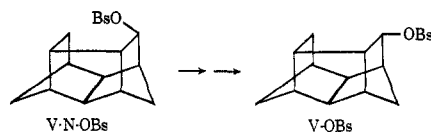
acetolysis, as is observed. The small amount of endo brosylate to exo brosylate isomerization in these cases is not directly detectable because of the pertinent exo/endo rate ratios. The exact extent of leakage between the k_s and k_Δ routes in VII-OBs and IX-OBs acetolyses are not apparent; minimum values of 10% in VII-OBs acetolysis and 7% in IX-OBs acetolysis are indicated.

Tanida and coworkers[5a,b] have found endo acetate and olefin formation in acetolysis of both *exo-* and *endo-*6,7-dinitrobenzonorbornen-2-yl brosylates and have stated[5b] that "the minor formation of endo acetates (products of retention) and olefins (products of elimination) from [the nitro- and dinitrobenzonorbornen-*endo*-2-yl brosylates] should be considered as *via* cationic intermediates." We note upon examination of the data of Tanida, *et al.*,[5a,b] that the ratios of the percentages of olefin to endo acetate formed in acetolysis at 180° of 6,7-dinitrobenzonorbornen-*exo*-2-yl brosylate (ratio 21:35) and of the endo brosylate (ratio 2.2:3.0) are the same within experimental error. Thus, formation of *ca.* 9% of exo brosylate *via* ion pair return in acetolysis of the endo brosylate would account for the formation of *ca.* 2% of olefin by a concerted cis elimination and *ca.* 3% of endo acetate by classical solvolysis.

Experimental Section

Melting points are corrected. Standard acetolysis procedures were employed.[16]

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-6-one (VI-Ketone).—A mixture of 1.0 g of VI-OH, mp 76–77° (lit.[4] mp 76.2–77.6°), in 50 ml of ether and 10 g of chromium trioxide in 50 ml of water was stirred vigorously for 4 hr. Then 50 ml of pentane was added, and the organic layer was washed with water until it was colorless. Distillation of the solution at 0.05 mm gave 0.7 g of oil that slowly solidified to a white solid, mp 32–34°.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.10. Found: C, 82.68; H, 8.13.

Similar oxidation of 100 mg of VII-OH, mp 71–72° (lit.[4] mp 71.5–72.6°), left from the original work,[4] gave 50 mg of solid ketone, mp 32–34°, mmp 32–34°. The ir spectra of both samples of ketone were identical.

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-*exo*-6-yl *p*-Bromobenzenesulfonate (VI-OBs).—VI-OBs, mp 100–101° (lit.[4] mp 97–98°), was prepared from VI-OH, mp 76–77° (lit.[4] mp 76.2–77.6°), that was 100% pure (analysis by gc of alcohol and derived acetate).

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-*endo*-6-yl *p*-Bromobenzenesulfonate (VII-OBs).—VII-OBs, mp 104–106° (lit.[4] mp 105–106°), was prepared from VII-OH, mp 72–73° (lit.[4] mp 71.5–72.6°), that was 100% pure (analysis by gc of alcohol and derived acetate).

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-*exo*-5-yl *p*-Bromobenzenesulfonate (VIII-OBs).—VIII-OBs, mp 91–92° (lit.[4] mp 91–92°), was prepared from VIII-OH, mp 48–50° (lit.[4] mp 49.5–51.5°), that was 100% pure (gc analysis).

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-5-one (VIII-Ketone).—Oxidation of 230 mg of VIII-OH from the original work[4] gave 200 mg of colorless liquid that contained less than 0.1% residual alcohol (gc analysis).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.10. Found: C, 82.66; H, 8.25.

Decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-*endo*-5-ol (IX-OH).—Reduction of the ketone from VIII-OH with excess lithium aluminum hydride in ether gave a solid alcohol mixture that consisted of 8.8% VIII-OH and 91.2% IX-OH (gc analysis). Chromatography of 0.24 g of alcohol mixture on a 2 × 52 cm column of activity 2.5 alumina with 10% ether in hexane gave 0.16 g of pure IX-OH (gc analysis indicated <0.5% VIII-OH

present) as an oil. Crystallization of the oil from pentane at −10° gave solid IX-OH, mp 66.0–67.5°.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.73; H, 8.95.

IX-OBs had mp 104–106°.

Anal. Calcd for $C_{18}H_{19}SO_3Br$: C, 54.68; H, 4.84. Found: C, 54.69; H, 4.82.

VI-OBs Acetolysis Products.—A 50-ml solution (0.0101 *M* VI-OBs) prepared from 0.2004 g of VI-OBs and acetic acid (0.0200 *M* sodium acetate) was held at 50° for 4.16 hr (20 half-lives). The solution was cooled, diluted with 50 ml of pentane, and extracted with 100 ml of water. The water layer was extracted with 30 ml of pentane. The pentane layers were combined, extracted with three 25-ml portions of saturated sodium bicarbonate solution and 50 ml of water, dried (Na_2SO_4), and concentrated to 2 ml with use of a $^8/_8$ × 14 in. column packed with glass helices. Gc analysis on a $^1/_4$ in. × 4 m column packed with 5% DOW X2405 on Chromosorb W, 80–100 mesh, at 155° and 30-psi helium pressure, indicated the product mixture to consist of 65.3 ± 1.5% VI-OAc (retention time 65 min), 27.3 ± 1.5% VII-OAc (retention time 59 min), and 7.4 ± 0.5% twisted monoene (retention time 5.6 min).

The product mixture was treated with excess lithium aluminum hydride in ether. The resultant products were examined on a $^1/_4$ in. × 2 m column of 10% UCON 50-HB 2000 on Chromosorb W, 60–80 mesh, at 180° and 30-psi helium pressure. There was <0.03% XII-OH and <0.03% V-OH (none detected). Under these analytical conditions, 0.03% XII-OH in VI-OH could be reproducibly detected.

VII-OBs Acetolysis Products.—A 25-ml solution (0.0102 *M* VII-OBs) was prepared from 0.1007 g of pure VII-OBs and acetic acid (0.0200 *M* sodium acetate) and was held at 50° for 3.82 hr (20 half-lives). The solution was worked up and analyzed as in the VI-OBs product study. There was 96.3% VI-OAc, 3.1 ± 0.3% VII-OAc, and 0.6 ± 0.2% twisted monoene. Gc analysis of the derived alcohol fraction revealed that <0.03% XII-OH and <0.03% V-OH were present (none detected).

A similar experiment in which 0.02 *M* tetrabutylammonium brosylate was incorporated gave an identical product mixture.

VIII-OBs Acetolysis Products.—A 25-ml solution (0.0100 *M* VIII-OBs) prepared from 98.6 mg of VIII-OBs and acetic acid that contained 0.0200 *M* sodium acetate was held at 50° for 14.46 hr (20 half-lives). After work-up, gc analysis on an NMPN column revealed the product mixture to consist of 93.3% acetates and 6.7% twisted monoene (2,3,3a,4,6a,7,7a-octahydro-2,4,7-metheno-1H-cyclopenta[a]pentalene), with <0.07% bird-cage hydrocarbon (decahydro-1,5,2,4-ethanediylidenecyclopenta-[cd]pentalene; none detected).

The product mixture was treated with 0.2 g of lithium aluminum hydride in 15 ml of ether. After the usual work-up, the alcohol fraction was analyzed by gc on a $^1/_8$ in. × 20 ft column packed with 2% UCON 50-HB 2000 on Chromosorb W, 80–100 mesh, at 150° and 50 psi of nitrogen, and was found to consist of 97.2% VIII-OH (retention time 49 min) and 2.8% IX-OH (retention time 52 min). There was <0.03% XII-OH (none detected); there was a peak with the same retention time as V-OH with 0.006% of the area of the VIII-OH peak.

IX-OBs Acetolysis Products.—A 5-ml solution (0.00988 *M* IX-OBs) prepared from IX-OBs and acetic acid (0.0200 *M* sodium acetate) was held at 50° for 50 hr (*ca.* 20 half-lives). After work-up, gc analysis on a $^1/_4$ in. × 2 m column packed with 25% NMPN revealed that the product mixture contained 99.47% acetates and 0.53% twisted monoene, with <0.05% bird-cage hydrocarbon (none detected).

The acetates were converted to alcohols with excess lithium aluminum hydride in ether. Gc analysis for IX-OH as in the VIII-OBs product study showed the alcohol fraction to consist of 99.75% VIII-OH and 0.25 ± 0.10% IX-OH.

1,2,3,4,4a,5,8,8a-Octahydro-*endo,endo*-1,4:5,8-dimethano-naphthalen-*exo*-2-ol (X-OH).—Hydroboration-oxidation[17] of purified isodrin in THF gave hexachloro-X-OH, mp 220–224° (lit.[18] mp 222° dec), in 74% yield. To a solution of 25 g (0.0653 mol) of the chlorinated alcohol and 158 g (2.13 mol) of *tert*-butyl alcohol in 400 ml of THF (distilled from LiAlH₄) under nitrogen in a 5-l. flask was added 30 g (4.3 g-atoms) of lithium wire cut

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

(17) (a) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961); (b) H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

(18) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, **82**, 5377 (1960).

into 0.5-in. lengths so as to allow the freshly cut pieces to fall directly into the flask. The mixture was stirred vigorously. 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 mixture was stirred until the spontaneous reflux subsided, then was heated at reflux for another 30 min, and then was poured while hot through a wire screen (to remove residual lithium). The solution was cooled, diluted with ice water, and extracted with ether. The organic solution was concentrated under aspirator vacuum and steam bath heat. Two crystallizations of the residue from hexane gave 5.0 g of pure (nmr analysis, quantitative hydrogenation assay) X-OH, mp 103.0–103.6° (lit.[19] mp 98–100°, lit.[20] mp 102.5–103.5°). **X-OAc**, mp 42.5–43.5°, was prepared by treatment of X-OH with acetic anhydride in pyridine at 5° for 3 days.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.02; H, 8.33. Found: C, 77.15; H, 8.61.

X-OBs.—To a frozen solution of 1.00 g (5.68 mmol) of X-OH in 10 ml of pyridine was added 1.66 g (6.50 mmol) of powdered brosyl chloride, and the flask was tightly stoppered. The pyridine was allowed to melt, and solution of the brosyl chloride was effected with swirling; the temperature of the mixture was kept well below 0° with intermittent cooling in Dry Ice–acetone. After complete solution was attained, the reaction mixture was placed in a dewar flask filled with Dry Ice. The dewar flask was lightly stoppered. After 36 hr, the frozen reaction mixture was allowed to melt and was added to 750 ml of pentane. The mixture was swirled vigorously for 3 min and filtered. The filtrate was rapidly concentrated adiabatically under vacuum. The residual pyridine was removed under vacuum while the flask was maintained in an ice bath. The white solid brosylate was dissolved in 210 ml of methylcyclohexane at room temperature, the mixture was filtered, and the filtrate was cooled in Dry Ice–acetone for crystallization. The resultant solid was collected by filtration and was washed well with pentane. There was obtained 0.90 g of X-OBs that had no odor (neither brosylic acid nor brosyl chloride was present). The X-OBs was used immediately as it is extremely unstable (a small sample developed the odor of brosylic acid within 5 min at room temperature). This sample of X-OBs contained less than 1% X-OH, as evidenced by there being less than 1% X-OH in the alcohols derived from the acetolysis products.

X-OBs Acetolysis Rate.—X-OBs was prepared in the usual way; because of its extreme reactivity, the brosylate was not dried well after the pentane wash performed after collection by filtration. A 24.8-mg quantity of the brosylate was rapidly weighed out and was added to 5 ml of acetic acid that contained 6 drops of indicator solution and 1.000 ml of a titrant solution that consisted of 0.02000 *M* sodium acetate in acetic acid. The acetic acid was at room temperature, 27 ± 1°. Complete solution was attained in *ca.* 15 sec. The indicator changed color 12 sec after the addition of the brosylate. The solution was titrated at various time intervals, and was held at 75° for 75 min for the final infinity determination (see Table II).

A plot of log T_∞ − log $(T_\infty - T)$ *vs.* time was made, and extrapolation of the straight line portion after 200 sec gave an intersection of 0.332 on the log axis at zero time; this value corresponds to a first infinity titer of 1.51 ml. This titer, 53.5% of the final infinity titer, was taken as the first infinity for calculation of the X-OBs total rate constant from zero time to 35 sec.

X-OBs Acetolysis Products after 100% Acid Production.—X-OBs was prepared by the low-temperature method from 0.50 g of X-OH and 0.83 g of brosyl chloride in 5 ml of pyridine. Immediately after isolation, the 0.40 g of X-OBs was added to 100 ml of acetic acid (that contained 0.020 *M* sodium acetate) at room temperature; the resultant solution was 0.0101 *M* in X-OBs. After 100 sec, the solution was placed in a 50° bath and held there for 15 hr (21 half-lives of VIII-OBs). The solution was cooled and worked up as usual. Gc analysis on an NMPN column showed the product mixture to consist of 24.1% bird-cage hydrocarbon, 1.7% twisted monoene, and 74.2% acetates.

(19) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).
(20) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

TABLE II
X-OBs RATE AT 27 ± 1°

Time, sec	Titer, ml	$10^4 k$,[a] sec^{-1}
0	sample added	
12	1.000	
35	1.47	1040.0
55	1.51	
85	1.53	
205	1.57	2.62
395	1.61	2.06
840	1.77	2.74
1125	1.81	2.36
1380	1.86	2.27
1580	1.91	2.32
1920	1.97	2.25
∞	2.825[b]	

[a] See text for method of calculation of the first rate constant, $k = 0.104$ sec^{-1}. The subsequent rate constants are based on integration from 85 sec; average $k = (2.37 \pm 0.17) \times 10^{-4}$ sec^{-1}. [b] 90.2% of theory.

A small portion of the product mixture was treated with excess lithium aluminum hydride in ether. Gc analysis on a UCON 50-HB 2000 column showed the alcohol fraction to consist of 62.4% VI-OH plus VII-OH plus VIII-OH, 5.48% XII-OH, and 32.1% V-OH. There was <1% X-OH and <0.2% of the endo epimer of X-OH.

The remainder of the acetolysis product mixture was analyzed by nmr in carbon tetrachloride solution. Integration over the α-proton region revealed the acetate portion to consist of 32.1% V-OAc, 41.6% VI-OAc, 5.8% VII-OAc, and 20.5% VIII-OAc plus XII-OAc.

From the combined gc and nmr data, the total acetolysis product composition from X-OBs is calculated to be 24.1% bird-cage hydrocarbon, 1.7% twisted monoene, 23.8% V-OAc, 30.9% VI-OAc, 4.3% VII-OAc, 11.1% VIII-OAc, and 4.1% XII-OAc.

X-OBs Acetolysis Products after 95% Reaction (Solvolysis Plus Rearrangement).—Immediately after it was prepared, 0.873 g of X-OBs was added to 100 ml of acetic acid (0.050 *M* sodium acetate) at 28°. The mixture was vigorously swirled, and the brosylate dissolved in *ca.* 15 sec. After an additional 15 sec the solution was poured into 500 ml of pentane. The pentane was rapidly extracted with 200 ml of water, three 150-ml portions of saturated sodium bicarbonate solution, and 200 ml of water. The pentane layer was dried (Na_2SO_4), and a small portion of it was passed through a short column of alumina to remove the brosylates and acetates. The column was washed with pentane, and the combined eluents were concentrated to 2 ml and analyzed by gc on an NMPN column. The hydrocarbon product consisted of 99.6% bird-cage hydrocarbon and 0.4% twisted monoene.

The remainder of the pentane solution containing all the acetolysis products was concentrated adiabatically under vacuum with a rotary evaporator. The residue was examined immediately in carbon tetrachloride solution by nmr. Integration over the aromatic proton region and over the α-proton region revealed that the substitution products (brosylates and acetates) consisted of 31.2% V-OBs, 18.4% V-OAc, 23.9% VI-OBs plus VIII-OBs, and 26.5% VI-OAc plus VIII-OAc plus XII-OAc. A series of simultaneous equations was set up from these data and from the product composition data for acetolysis of VI-OBs, VIII-OBs, X-OBs after 100% acid production, and V-OBs (38% bird-cage hydrocarbon, 1.3% twisted monoene, 34.8% V-OAc, 9.8% VI-OAc, 2.1% VII-OAc, 12.8% VIII-OAc, 1.2% XII-OAc; revised analyses by gc and nmr methods). Solution of the equations gave the direct products from X-OBs acetolysis: 14.5% bird-cage hydrocarbon, 0.06% twisted monoene, 25.3% V-OBs, 15.0% V-OAc, 14% VI-OBs, 19% VI-OAc, 5.4% VIII-OBs, 3% VIII-OAc, and 3.8% XII-OAc.

Registry No.—VI-ketone, 34220-07-0; VIII-ketone, 34220-08-1; IX-OH, 34226-03-4; IX-OBs, 34226-04-5; X-OAc, 34226-05-6; X-OBs, 34226-06-7.