TABLE III
RR'NCOCHBrCH$_2$CH$_2$CHBrCONRR'

Compd	R	R'	Mp,[a] °C	Empirical formula[b]	Ir (cm^{-1})[c] NH	Ir (cm^{-1})[c] C=O
a	Phenyl	H	243	$C_{18}H_{18}Br_2N_2O_2$	3300	1660
b	*p*-Tolyl	H	236	$C_{20}H_{22}Br_2N_2O_2$	3260, 3300	1660, 1700
c	*p*-Anisyl	H	238	$C_{20}H_{22}Br_2N_2O_4$	3280, 3300	1660, 1690
d	*p*-Nitrophenyl	H	239	$C_{18}H_{16}Br_2N_4O_6$	3290, 3320	1680, 1700
e	*p*-Chlorophenyl	H	246	$C_{18}H_{16}Br_2Cl_2N_2O_2$	3270, 3300	1660, 1700
f	*m*-Chlorophenyl	H	220	$C_{18}H_{16}Br_2Cl_2N_2O_2$	3280, 3310	1660, 1700
g	2-Methyl-4-chlorophenyl	H	244	$C_{20}H_{20}Br_2Cl_2N_2O_2$	3270	1660
h	Phenyl	CH_3	161	$C_{20}H_{22}Br_2N_2O_2$		1670

[a] All compounds, except Ih, decompose at the melting point. [b] Satisfactory analytical values for C, H, N, and halogen as appropriate (±0.35) were reported for all compounds in the table: Ed. [c] Ir spectra in Nujol mulls.

Registry No.—Ia, 27062-59-5; Ib, 27062-60-8; Ic, 27062-61-9; Id, 27062-62-0; Ie, 27062-63-1; If, 27062-64-2; Ig, 27062-65-3; IIb, 27062-66-4; *trans,trans*-IIc, 27062-67-5; *cis,trans*-IIc, 27062-68-6; IIg, 27062-69-7; IIIa, 27062-70-0; IIIb, 27062-71-1; IIIc, 27062-72-2; IIIe, 27062-73-3. Table III—a, 27062-74-4; b, 27062-75-5; c, 27062-76-6; d, 27062-77-7; e, 27062-78-8; f, 27062-79-9; g, 27062-80-2; h, 27062-81-3.

The Synthesis and Acetolysis of 6-Oxabicyclo[3.2.1]octane-1-methyl *p*-Bromobenzenesulfonate[1]

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The intramolecular oxymercuration of 4,4-bis(hydroxymethyl)-1-cyclohexene (**2**) followed by sodium borohydride reduction of the chloromercurial gave 1-hydroxymethyl-6-oxabicyclo[3.2.1]octane (**4a**). The brosylate **5a** derived from this alcohol was solvolyzed in acetic acid. The products included the unrearranged acetate **6**, 4,4-bis(acetoxymethyl)-1-cyclohexene (**7a**), and the two ring-expanded bridgehead acetates **8** and **9**. Sodium borodeuteride reduction of the oxabicyclic chloromercurial gave 1-hydroxymethyl-6-oxabicyclo[3.2.1]octane-4-*d* (**4b**). The brosylate **5b** of this alcohol was also solvolyzed in acetic acid. The 4,4-bis(acetoxymethyl)-1-cyclohexene isolated from this acetolysis had lost approximately 50% of the deuterium originally located in the brosylate. The nature of the solvolytic rearrangements and the significance of the results of the deuterium experiments are discussed.

Numerous investigations of the solvolyses of bicyclic bridgehead methanol derivatives have been reported.[3-10] These studies have enhanced our understanding of bond-angle deformation and polar effects on reactivity in constrained neopentyl-type systems, particularly as regards the influence of these effects on 1,2- and 1,3-cationic rearrangements and fragmentations. The study of norbornenyl-1-carbinyl derivatives by Wilt and coworkers[8] has served to define the geometrical requirements for homoallylic delocalization. Their work in this system has provided a measure of the inductive (or field) effect of a vinyl group β to the solvolyzing center uncomplicated by homoallylic delocalization. Similar considerations led us to the investigation of the title bicyclic system in order to determine the effects of carbon–oxygen dipoles on solvolyses at the 1-carbinyl position.

In the solvolyses of compounds containing an alkoxyl group as a substituent elsewhere in the molecule, it is often difficult to assess the inductive (or field) effect of a C–O dipole on the cationic reaction center since appropriately located alkoxyl groups can facilitate solvolysis by intramolecular attack to form cyclic oxonium ions.[11-13] This competing process is eliminated in solvolyses of compounds such as **5a**. Furthermore, the precise orientation of the O–C bonds is held relatively fixed with respect to the reaction center and can be estimated with a high degree of certainty. It was also of interest to learn whether a 1,3-hydride shift from C-7 to the solvolyzing center would be observable in view of the potential cation-stabilizing effect of the ether oxygen.

Results

Syntheses.—The title brosylate **5a** and its deuterated analog **5b** were prepared using a four-step sequence

(1) Abstracted in part from the thesis of R. A. Froehlich, submitted to San Diego State College in partial fulfillment of the requirements for M.S. Degree, Sept 1969.

(2) National Science Foundation High School Teacher Research Participant, 1967.

(3) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(4) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

(5) R. S. Bly and Q. E. Cooke, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, Abstract 80-S; R. S. Bly and E. K. Quinn, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract 91-O.

(6) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connar, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(7) W. D. Closson and G. T. Kwiatowski, *ibid.*, **21**, 2779 (1965).

(8) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

(9) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 1014 (1968).

(10) S. H. Graham and D. A. Jonas, *J. Chem. Soc. C*, 188 (1969).

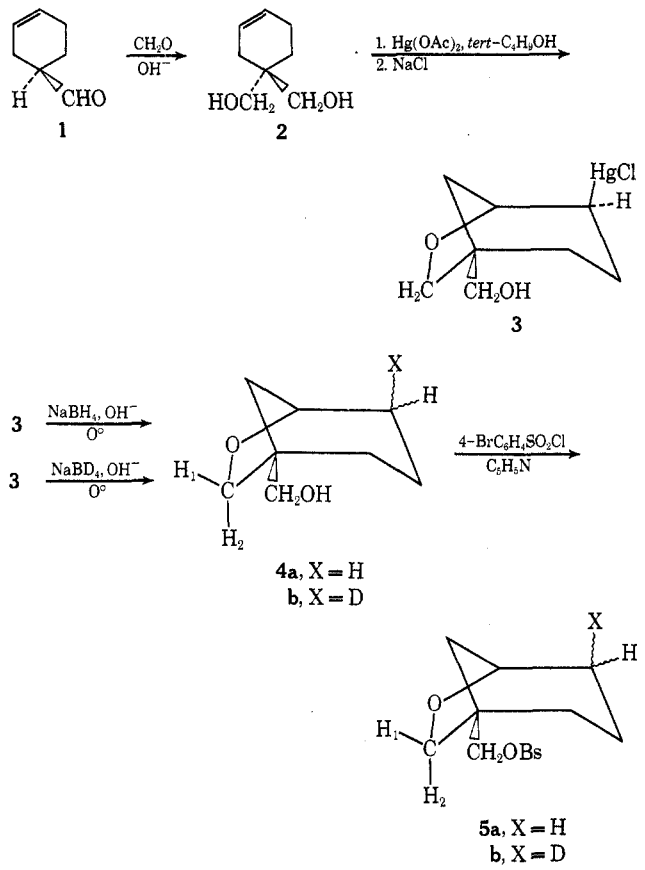
(11) E. L. Allred and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 3991, 3998, 4008, 4012 (1967).

(12) P. W. Austin, J. G. Buchanan, and D. G. Large, *Chem. Commun.*, 418 (1967).

(13) D. S. Noyce, B. R. Thomas, and B. N. Bastian, *J. Amer. Chem. Soc.*, **82**, 885 (1960); D. S. Noyce and B. N. Bastian, *ibid.*, **82**, 1246 (1960).

starting from the commercially available 3-cyclohexene-1-carboxaldehyde (**1**) as shown in Scheme I.

SCHEME I



1 2 3

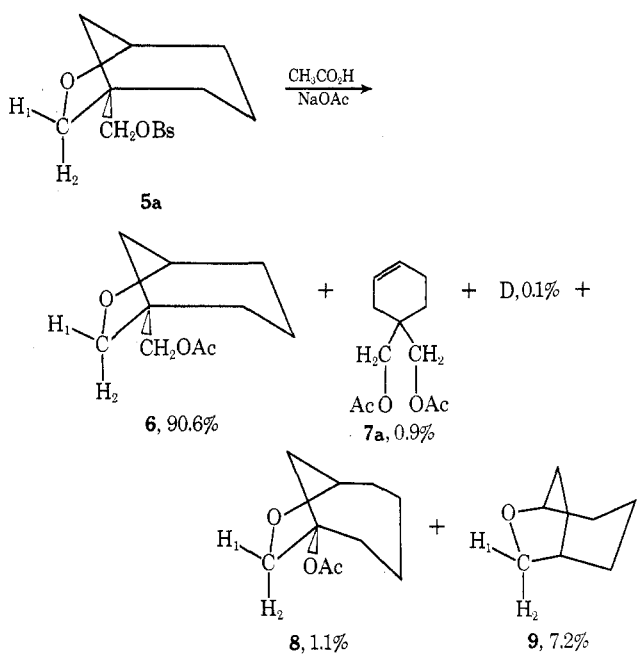
4a, X = H
b, X = D

5a, X = H
b, X = D

The intramolecular oxymercuration of **2** was suggested by the related ring closure of 4-methylenecyclohexanemethanol to chloromercurimethylnorcineole reported by Weinberg and Wright.[14] In principle, the cyclization of **2** can lead to two isomers possessing respectively the [2.2.2] and the [3.2.1] bicyclic skeleton. In the present study only one product could be isolated and no evidence for the presence of a second isomer was obtained. That the ring-closed oxabicyclic product isolated possessed the [3.2.1] ring system was clearly demonstrated by the nmr spectrum of **4a**. The protons at the 7 position appear as an AB doublet of doublets with calculated chemical shifts of 3.67 and 3.82 ppm. It is clear that the methylene protons α to the ether oxygen would be magnetically equivalent in the [2.2.2] isomer.[15] The C–Hg bond of the chloromercurial **3** would be expected to be axially oriented since oxymercurations of cyclohexene are known to proceed stereospecifically trans.[21–23] The borohydride reduction of **3** under basic conditions gave **4a** in reasonably good yield. However, the desired product was accompanied by approximately 20% of **2**, the deoxymercuration product. Bordwell and Douglass[24] carried out sodium borohydride reduction demercurations on a wide variety of β-oxy mercurials. Under basic conditions these reductions were reportedly free of deoxymercuration. For example, *trans*-2-methoxy-1-chloromercuricyclohexane was reduced to cyclohexyl methyl ether in 86% yield with no evidence for the presence of cyclohexene. The modest amount of strain in **3** may contribute to the ease of this ring-opening demercuration; however, the postulated mechanism[24] for previous reductive deoxymercurations normally observed at pH 7 or below (and requiring protonation of the β oxygen) would appear to require modification in this case. The brosylate **5a** was prepared by the usual method. The monodeuterated analogs **4b** and **5b** were prepared for purposes discussed below.

Acetolyses.—The brosylate **5a** was solvolyzed in boiling acetic acid containing a 20% molar excess of anhydrous sodium acetate to give a 91% yield of products. The glpc analysis showed the presence of five products which were isolated by preparative glpc. Four of the compounds were in sufficient quantity to be identified (see Scheme II). Compounds **6** (the main product) and **7** were identified by comparison with authentic samples. Compounds **8** and **9** were identified by elemental, glpc, infrared, nmr, and mass spectral analyses. In the nmr spectra, the increase in the integrated areas upfield from about 2.0 ppm (as compared with **5a** or **6**) coupled with the disappearance of the methylene singlet

SCHEME II



5a

6, 90.6%

7a, 0.9%

8, 1.1%

9, 7.2%

(14) N. L. Weinberg and G. F. Wright, *Can. J. Chem.*, **43**, 24 (1965).

(15) The [3.2.1] bicyclic hydrocarbon system (as well as the oxabicyclic analog) appears to be thermodynamically more stable than the [2.2.2] system.[16–19] However, it is interesting to note that a carbonyl group in these oxabicyclic ring systems may change the thermodynamic preference. Noyce, Weingarten, and Dolby[20] observed that the lactone of *cis*-3-hydroxycyclohexanecarboxylic acid rearranges to the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid. However, the latter isomer was isolated in relatively low yield and no other product in the reaction mixture was characterized.

(16) W. von E. Doering and M. Farber, *J. Amer. Chem. Soc.*, **71**, 1514 (1949).

(17) M. S. Newman and Y. T. Yu, *ibid.*, **74**, 507 (1952).

(18) N. Wendler, D. Taub, and C. H. Kuo, *J. Org. Chem.*, **34**, 1510 (1969).

(19) A. Isard and F. Weiss (to Ugine Kuhlmann), French Patent 1,514,315 (1968); *Chem. Abstr.*, **70**, 87552y (1969).

(20) D. S. Noyce, H. I. Weingarten, and L. J. Dolby, *J. Org. Chem.*, **26**, 2101 (1961).

(21) M. M. Kreevoy and F. R. Kowitt, *J. Amer. Chem. Soc.*, **82**, 739 (1960).

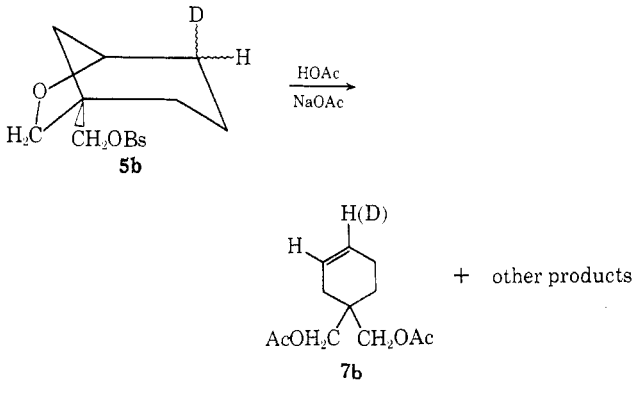
(22) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(23) Surprisingly, the *A* value of the bromomercuri group is zero within experimental error (±5%) with a probable small preference for the axial orientation [F. R. Jensen and L. H. Gale, *ibid.*, **81**, 6337 (1959)].

(24) F. G. Bordwell and M. L. Douglass, *ibid.*, **88**, 993 (1966).

(-CH_2O- at C-1) indicates ring expansion in the rearranged acetates. Furthermore, the persistence of the AB doublet of doublets (see Experimental Section) in **8** and **9** shows that ring expansion did not involve the methylenoxy bridge. In agreement with structures **8** and **9**, the chemical shifts for the protons H_1 and H_2 (Scheme II) are shifted downfield (compared with H_1 and H_2 in **6**) by magnitudes ranging from 0.14 to 0.34 ppm. These protons are now bound to carbons with oxygen functions at both the α and β positions. The magnetic environments of the bridgehead protons (C-6 H in **8** and C-5 H in **9**) are nearly identical with chemical shifts at 4.48 and 4.47 ppm, respectively. This represents a very small downfield shift of approximately 0.04 ppm compared with **6**. Although 1,3-hydride shifts in a related system have been reported,[10] structures for **8** and **9** resulting from similar 1,3-hydride shifts from C-2, C-7, or C-8 to the primary carbon bearing the departing brosylate group or from ring expansion followed by a 1,2-hydride shift can be excluded. The former case would require a *C*-methyl singlet near 1 ppm which is not observed. The latter possibility can be ruled out by the observation that no new absorption below 2.5 ppm is found in the nmr spectrum of either **8** or **9**. The structures for **8** and **9** have been tentatively made as indicated on the following basis. A multiplet (roughly appearing as a broadened, unsymmetrical doublet) is found well separated and downfield from the remaining methylene protons at approximately 2.35 ppm in **8**. The integral of this absorption corresponds to two protons. This is probably due to the two protons on the single methylene bridge. It will be noted that this C-9 position is now β to two oxygen functions, although conformational changes in the orientation of the acetate carbonyl (and its spacial relationship to the methylene bridge protons) may be causing this difference in chemical shift of **8** compared to **9**. A second notable difference between the nmr spectra of **8** and **9** is seen in the doublet of doublets attributable to the protons labeled H_1 and H_2 in either **8** or **9**. The difference in chemical shift ($\Delta\delta$) between the two doublets in **8** is 0.38 ppm while the same difference in **9** is only 0.16 ppm. From gross structural considerations it would appear likely that the protons H_1 and H_2 in **8** would experience greater differences in magnetic environment than would H_1 and H_2 in **9**. Again, the conformational preference of the acetoxy carbonyl group in these two compounds may be important.

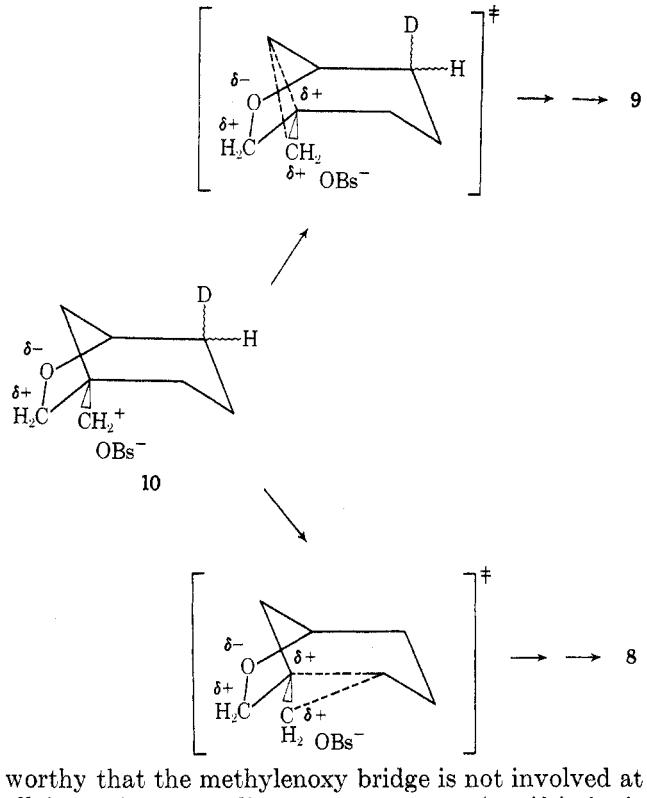
The acetolysis of **5b** was conducted under conditions identical with those used for **5a**. The 4,4-bis(acetoxymethyl)-1-cyclohexene (**7b**) was isolated by preparative glpc and analyzed for deuterium content using both nmr and mass spectrometric methods. The starting brosylate **5b** was monodeuterated to the extent of 90.6%. The olefinic diacetate **7b** isolated was 47 ± 3% monodeuterated.



5b **7b**

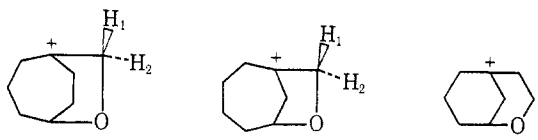
Discussion

One of the most striking observations made in this solvolytic study is the remarkably small amount of rearrangement which occurs. Although the bicyclo[3.2.1]octane-1-methyl brosylate itself has not yet been prepared for parallel studies, it is interesting to compare the present results with those reported by Graham and Jonas.[10] Under conditions similar to those employed here, bicyclo[3.3.1]nonane-1-methyl brosylate solvolyzes with 36% of the product rearranged through ring expansion. Presumably the rearrangement products **8** and **9** found in the acetolysis of **5a** are generated by a 1,2 migration of an initially formed ion pair **10** (although concerted migration and loss of OBs^- cannot be ruled out). If one considers the partial positive charge (result of C–O dipole) residing on the carbon (C-7 of the brosylate) adjacent to the new center of developing charge (C-1), it is not surprising that these paths are relatively energetically unfavorable. It is also noteworthy that the methylenoxy bridge is not involved at all in a ring-expanding rearrangement (or, if it is, it cannot account for more than 0.1% of the acetolysis product). This is reminiscent of the absence of vinyl migration in the hydrolysis of norbornenyl-1-carbinyl tosylate.[8] The lack of proclivity toward rearrangement of these two "groups" may be related. It is generally accepted that in 1,2-cationic rearrangements a migrating carbon bears a portion of the total positive charge. The cationic character of the migrating group is probably fairly substantial in Baeyer–Villiger rearrangements,[25] but in carbon to carbon rearrangements



(25) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Amer. Chem. Soc.*, **80**, 6393 (1958); J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

the charge on the migrating carbon may be considerably less.[26] Nonetheless, an attractive explanation for the absence of alkoxymethylene migration in the acetolysis of **5a** may derive from the fact that for migration to occur some charge delocalization onto the migrating carbon is important. Since the methylenoxy carbon already bears substantial charge in **10**, it would be energetically unfavorable for it to accept additional charge. And π-electron delocalization of charge by oxygen would appear to be unavailable on geometrical grounds.[27] To the extent that the three cations **11**, **12**, and **13** can serve as models for the transition



11 **12** **13**

states for the three possible migrations of carbon, an examination of their relative strain may be instructive. A consideration of the framework molecular models of **11**, **12**, and **13** (with sp^2 hybridization at the positively charged bridgehead carbons and sp^3 hybridization elsewhere) suggests that **12** would possess the greatest amount of angle strain and destabilization from nonbonded interactions. The ions **11** and **13** would clearly be more stable on both counts, although a choice between **11** and **13** as the least stable ion cannot be made with certainty. Thus the assignment of structures for compounds **8** and **9** (considering their relative yields) is in accord with predictions based upon comparisons of ions **11** and **12**. The retardation of migration of the oxymethylene bridge in **5a** is probably less a result of ring strain in the transition state leading to **13** than of the type of charge interactions suggested above. This is in agreement with the results of a recent study of the buffered acetolysis of bicyclo[3.2.1]octane-1-methyl *p*-toluenesulfonate.[28] The acetolysis leads to the formation of two products: 1-acetoxybicyclo[3.2.2]nonane and 1-acetoxybicyclo[3.3.1]nonane in a ratio of about 2:1. Clearly, ring expansion of the two-carbon bridge in this "hydrocarbon" analog of the oxabicyclic system is competitive with ring expansion of the one-carbon bridge. If ions such as **11** and **12** (or corresponding ion pairs) are intermediates in the acetolysis of **5a**, they might be expected to undergo rapid 1,2-hydride shifts of H_1 or H_2. Such a shift would lead to an ion stabilized by the adjacent oxygen. Considering the stabilities of the corresponding hydrocarbon bicyclic bridgehead olefins[29] such a rearrangement would be more likely for **12** than for **11**. Future solvolyses under conditions expected to give larger amounts of rearrangement may yet reveal this type of shift.

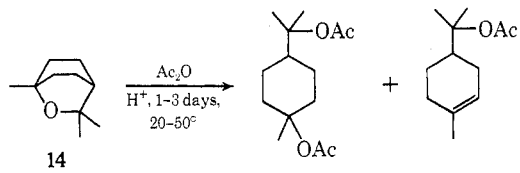
(26) See J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 3240 (1968); J. R. Owen and W. H. Saunders, Jr., *ibid.*, **88**, 5809 (1966).

(27) An ether oxygen can usually stabilize a cation forming on an adjacent carbon through π delocalization of an electron pair (note, for example, accelerated rates of solvolyses of α-halo ethers). However, the oribital on C-7 (involved in C-7, C-1 bond) which could conceivably develop 2p character is nearly orthogonal to the orbital(s) of the unshared electrons on oxygen.

(28) Private communication. We thank Professor J. R. Wiseman for communicating these results to us.

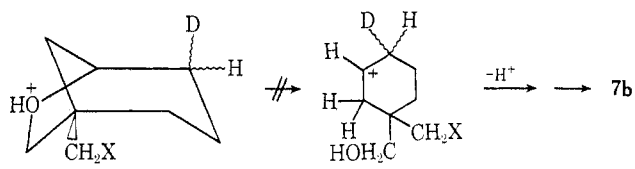
(29) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 957 (1970), and references therein; see also J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967).

An unexpected acetolysis product from **5a** was 4,4-bis(acetoxymethyl)-1-cyclohexene (**7a**). This diacetate presumably is formed *via* acid-catalyzed, ring-opening elimination and esterification. A few elimination reactions which involve loss of R–OH from an ether have been observed. They usually require strong acids and/or elevated temperatures.[30] An interesting example which bears a resemblance to the formation of **7a** is the ring opening of cineole (**14**) in acetic anhydride containing small amounts of sulfuric acid or ferric chloride.[31] In the hopes of learning more about the



14 50:50 mixture

elimination reaction forming **7a** and determining the stereochemistry of the borohydride reduction of **3**, the deuterated brosylate **5b** was subjected to acetolysis as before. As indicated above, the olefinic diacetate **7b** isolated had lost approximately 50% of the deuterium contained in the starting material. Regardless of the equatorial–axial distribution of deuterium in **5b**, this result removes from serious consideration one mechanistic possibility, namely ring opening to form a "free"



carbonium ion followed by proton loss. Were this the case, the deuterium content of **7b** would have been expected to be considerably higher. Furthermore, such a mechanism would lead to two isomeric olefinic diacetates. No evidence for the presence of a second diacetate was found, and the diacetate isolated from the solvolysis of **5a** was identical in all respects with that of an authentic sample of 4,4-bis(acetoxymethyl)-1-cyclohexene.

The mechanism and stereochemistry of borodeuteride reductions of organomercurials has been the subject of several investigations. Retention of configuration in the borodeuteride reduction of *exo-cis*-2-hydroxy-3-chloromercurinorbornane[24] and *trans*-2-hydroxycyclopentylmercuric acetate[32] has been observed. However, the earlier four-centered mechanism based upon the assumption that retention was general is not in agreement with recent observations of loss of stereochemistry[31] and the occurrence of radical-type rearrangements[32,33] during numerous other reductions of organomercurials. The synthetic sequence in Scheme I combined with the acetolysis of **5b** to form **7b** appeared to offer the possibility of determining the stereochemistry of the borohydride reduction of a chloromercurial group in a cyclohexyl system. If the reduction of **3** were stereospecific leading to deuterium in the axial position and the ring opening involves concerted attack by a base (such as

(30) R. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

(31) E. Knoevenagel, *Justus Liebigs Ann. Chem.*, **402**, 133 (1914).

(32) D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **91**, 719 (1969).

(33) G. A. Gray and W. R. Jackson, *ibid.*, **91**, 6205 (1969).

acetate ion), carbon–carbon double bond formation, and cleavage of the carbon–oxygen bond,[34] the deuterium analysis of the product would require that the attack by base be equally probable on an exo (axial) or endo (equatorial) hydrogen. However, most evidence in the literature indicates that β eliminations in cyclohexane derivatives are highly stereoelectronically controlled[35] with trans (antiperiplanar) eliminations predominating.[36] Consequently, this can be taken as evidence that the borodeuteride reduction of **3** is not stereospecific. This is in agreement with a previous observation of the absence of stereospecificity in the borodeuteride reductions of 4-methylcyclohexylmercuric halides.[37]

The extent to which the ring-opening elimination proceed from the brosylate **5** and the acetate **6** is unknown. However, it is interesting to note that, in the course of preparing **6** from the corresponding alcohol **4a** and acetic anhydride containing anhydrous sodium acetate, 17% of the ring-opened diacetate **7a** was formed.

Rate and product study comparisons of the title brosylate and tosylate with the parent bicyclo[3.2.1]-1-carbinyl derivatives and related studies in smaller bicyclic systems are planned or in progress.

Experimental Section[38]

4,4-Bis(hydroxymethyl)-1-cyclohexene (**2**) was prepared from 3-cyclohexene-1-carboxaldehyde employing the crossed Cannizzaro reaction, mp 90–91° (lit.[39] mp 92.0°).

1-Hydroxymethyl-4-chloromercuri-6-oxabicyclo[3.2.1]octane (**3**).—To a mixture of 45.3 g (0.142 mol) of mercuric acetate and 920 ml of dry *tert*-butyl alcohol (stirred for 10 min) was added in one portion 20.0 g (0.141 mol) of 4,4-bis(hydroxymethyl)-1-cyclohexene. The resulting mixture was stirred at room temperature for 49 hr. It was then clarified by filtration. To the clear filtrate was added 14.0 g (0.240 mol) of sodium chloride. The white precipitate which formed was collected on a funnel and washed with several 5-ml portions of water affording 39.1 g of **3**, mp 179–182°. A second crop (4.8 g) was obtained by concentrating the filtrate. The combined product was recrystallized from 95% aqueous ethanol affording 39.0 g (73%) of fine white crystals, mp 177–178°.

Anal. Calcd for $C_8H_{13}ClHgO_2$: C, 25.47; H, 3.47; Cl, 9.39. Found: C, 25.71; H, 3.80; Cl, 9.22.

1-Hydroxymethyl-6-oxabicyclo[3.2.1]octane (**4a**).—A mixture of 43.4 g (0.115 mol) of 1-hydroxymethyl-4-chloromercuri-6-oxabicyclo[3.2.1]octane and 80 ml of 5% aqueous sodium hydroxide was stirred for several minutes at 0°. A solution of 1.18 g (0.0312 mol) of sodium borohydride in 180 ml of cold, 10% aqueous sodium hydroxide was then added dropwise over a 20-min period. The resulting mixture was stirred at 0° for 1 hr and then subjected to continuous ether extraction. The ether extract was washed successively with 0.12 *N* hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water. The extract was dried and concentrated to 15.9 g of a yellow oil. The desired bicyclic product **4a** was contaminated with approximately 20% **2**. A sample of the oil (13.1 g) was chromatographed on a support mixture obtained by adding 30.2 g of silver nitrate dissolved in 100 ml of water to a mixture of 68.0 g of Celite and 412 g of 100 mesh silicic acid. The column was prepared from the thoroughly mixed support material in an ether–petroleum ether slurry. The desired product **4a** was eluted with ether as a colorless oil: 9.49 g (58% corrected for sample size used in separation); nmr ($CDCl_3$) 1.20–2.10 (m, 8 ring methylene protons), 2.93 (s, 1, –OH), 3.54 (s, 2, $-CH_2OH$), 3.67 and 3.82 (AB d of d,[40,41] 2, J_{AB} = 7.5 Hz, $-OCH_2C<$), 4.40 (broadened t, 1, C-5 H).

The 3,5-dinitrobenzoate of **4a** was prepared and melted at 104–105° (cor) (lit.[19] mp 100–101°). The nmr spectrum of the dinitrobenzoate ($DCCl_3$) revealed the following absorptions: 1.44–2.3 (m, 8, ring methylene protons), 3.74 and 3.96 (AB d of d,[40] 2, J_{AB} = 8 Hz, $-OCH_2C<$), 4.43 (s,[42] 2, $-CH_2O_2CAr$), 9.05–10.3 (m, 3, aromatic protons).

1-Hydroxymethyl-6-oxabicyclo[3.2.1]octane-4-*d* (**4b**).—The deuterated analog of **4a** was prepared by reducing 8.00 g (0.0212 mol) of the chloromercuri derivative **3** with 0.220 g (0.00526 mol) of sodium borodeuteride using the conditions previously described. The crude product was chromatographed using the silicic acid–Celite–silver nitrate column previously described and eluting with 20% by volume petroleum ether (bp 30–60°) in diethyl ether. The separation afforded 0.458 g of **2** and 1.613 g (54%) of **4b** (obtained as a colorless oil). The nmr spectrum of **4b** ($CDCl_3$) revealed the following features: 1.25–2.10 (m, 7 ring methylene protons), 2.98 (s, 1, –OH); 3.51 (s, 2, $-CH_2OH$), 3.64 and 3.80 (AB d of d,[40,43] 2, J_{AB} = 7.5 Hz, $-OCH_2C<$), 4.38 (broadened t, 1, C-5 H). The infrared spectrum ($CDCl_3$) of **4b** was very similar to that of the undeuterated analog **4a**. The major exception was a band at 2160 cm^{-1} (CD stretch) in **4b**. The mass spectrum (15 eV) of **4b** showed the weak parent ion at *m/e* 143 (5.5) and major peaks at 112 (100), 95 (8.8), and 82 (3.4). Using the intensities of the ions at *m/e* 112 (P + 1) and 111 (P), the % deuteration was calculated to be 91%. The intense peak at *m/e* 112 corresponds to loss of $\cdot CH_2OH$ from the molecular ion.

6-Oxabicyclo[3.2.1]octane-1-methyl *p*-Bromobenzenesulfonate (**5a**).—The bicyclic alcohol **4a** (9.49 g, 0.0668 mol) was dissolved in 70 ml of cold (0°), freshly distilled pyridine. To the solution was added 23.0 g (0.0901 mol) of *p*-bromobenzenesulfonyl chloride. The resulting mixture was swirled to effect solution and was then allowed to stand for 15 hr at −3°. The solution was warmed to room temperature for 45 min, cooled again to 0°, treated with cold 6 *N* hydrochloric acid to neutralize, and extracted with chloroform. The extract was washed successively with water, 10% aqueous sodium carbonate, and finally water. It was dried and concentrated leaving 28.1 g of the crude brosylate **5a**. The crude brosylate was recrystallized from ether affording three crops of colorless crystals: first crop, 10.5 g, mp 95–96.5°; second crop, 4.81 g, mp 94.5–95.0°; third crop 1.93 g, mp 94–96° (total yield 72%). A sample recrystallized from ether for elemental analysis melted at 97.0–97.8°.

Anal. Calcd for $C_{14}H_{17}O_4BrS$: C, 46.56; H, 4.71; Br, 22.13. Found: C, 46.35; H, 4.61; Br, 22.38.

The nmr spectrum ($CDCl_3$) of the brosylate revealed the following absorptions: 1.10–2.0 (m, 8 methylene ring protons), 3.56 and 3.81 (AB d of d,[44] 2, J_{AB} = 7.5 Hz, $-OCH_2C<$), 3.98 (s, 2, $-CH_2OBs$), 4.40 (broadened t, C-5 H), 7.76 (s, 4, aromatic protons).

(34) The argument would also be true if ionization of the carbon–oxygen bond to form a vibrationally excited cation preceded loss of the proton (or deuteron at C-4).

(35) S. J. Cristol, *J. Amer. Chem. Soc.*, **69**, 338 (1947); S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951); E. D. Hughes, C. K. Ingold, and J. B. Rose, *J. Chem. Soc.*, 3839 (1953); S. J. Cristol and F. R. Stermitz, *J. Amer. Chem. Soc.*, **82**, 4962 (1960); C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

(36) A recent exception to this rule was recently reported by T. Cohen and A. R. Daniewski, *ibid.*, **91**, 533 (1969).

(37) Private communication. Unpublished results of Professor T. G. Traylor.

(38) All melting points and boiling points are uncorrected unless otherwise specified. The infrared spectra were determined on a Perkin-Elmer Model 621 grating spectrophotometer. Proton magnetic resonance spectra were determined on a Varian Model A-60 spectrometer. The chemical shifts are relative to tetramethylsilane used as an internal reference in the solvents cited. Mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Vapor phase chromatographic separations and analyses were effected using a Varian Aerograph Model 90-P gas chromatograph. Elemental analyses were performed by MHW Laboratories (Garden City, Mich.) or by Mr. C. F. Geiger (Ontario, Calif.). Deuterium analyses were performed by Josef Nemeth (University of Illinois) or mass spectrometrically by Mr. R. Steed (San Diego State College).

(39) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **70**, 946 (1948).

(40) Calculated chemical shifts: see L. M. Jackman and S. Sternhell, *Int. Ser. Monogr. Org. Chem.*, **5**, 129 (1969).

(41) The highest field component of the "quartet" is partially obscured by the singlet at 3.54.

(42) The C-5 H proton (presumably a broadened triplet) appears as broadening in the base of this singlet.

(43) The highest field component of the "quartet" is partially obscured by the singlet at 3.51.

(44) The two peaks constituting the higher field doublet are slightly broadened by secondary coupling of undetermined origin. The chemical shifts are calculated.[40]

6-Oxabicyclo[3.2.1]octane-4-*d*-1-methyl *p*-Bromobenzenesulfonate (5b).—The deuterated brosylate **5b** was prepared from 1.61 g (0.0113 mol) of the deuterated oxabicyclic alcohol (**4b**) and 4.09 g (0.0160 mol) of *p*-bromobenzenesulfonyl chloride using the conditions previously described. The crude product (3.08 g) was light yellow in color, mp 85–89°. The pure brosylate was obtained after two recrystallizations from ether as 2.46 g (60%) of colorless needles, mp 96–98°. The nmr spectrum ($CDCl_3$) of **5b** showed the following absorptions: 1.24–2.15 (m, 7, methylene ring protons), 3.52 and 3.80 (AB d of d,[44] 2, J_{AB} = 7.5 Hz, $-OCH_2C<$), 3.97 (s, 2, $-OCH_2OBs$), 4.37 (broadened t, C-5 H), 7.71 (s, 4, aromatic protons). The mass spectrum (80 eV) showed the very weak but characteristic molecular ions as a two-peak isotopic "cluster" at *m/e* 363 and 361 (0.8). The complex fragmentation ions included major peaks at *m/e* 157 and 155 (11) 125 (68), and 112 (100). Using the intensities of the ions at *m/e* 125 (P + 1) and 124 (P), the per cent deuteration was calculated to be 94%. A similar estimate using intensities of the *m/e* 112 (P + 1) and 111 (P) ions led to a value of 92%. The result of combustion analysis of the deuterated brosylate **5b** (by Mr. Josef Nemeth) was 5.33 atom % excess which corresponds to 90.6% monodeuteration.

1-Acetoxymethyl-6-oxabicyclo[3.2.1]octane (6).—A mixture of 0.220 g (0.00155 mol) of 1-hydroxymethyl-6-oxabicyclo[3.2.1]-octane, 0.174 g (0.00214 mol) of anhydrous sodium acetate, and 2 ml of acetic anhydride was allowed to stand overnight at room temperature and then boiled under reflux for 2.5 hr. The mixture was diluted with 20 ml of water, allowed to stand for 2 days, and then extracted with ether. The extract was washed successively with water, 10% aqueous sodium carbonate, and water. It was dried and concentrated to 0.181 g of a yellow oil consisting of approximately 83% **6** and 17% of a side product later shown to be the diacetate **7a**. A pure sample of **6** was collected by preparative glc (5 ft × 0.25 in., 20% silicon oil on Chromosorb W column).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.78; H, 8.74.

The nmr spectrum of **6** ($CDCl_3$) revealed the following features: 1.20–2.00 (m, 8 methylene ring protons), 2.08 (s, 3, CH_3CO_2-), 3.68 and 3.88 (AB d of d,[40] 2, J_{AB} = 7.5 Hz, $-OCH_2C<$), 4.05 (s, 2, $-CH_2OAc$), 4.44 (broadened t, 1, C-5 H). The infrared spectrum of **6** ($CDCl_3$) showed a strong band at 1730 cm^{-1} (ester C=O).

4,4-Bis(acetoxymethyl)-1-cyclohexene (7a).—A mixture of 0.500 g (0.00352 mol) of 4,4-bis(hydroxymethyl)-1-cyclohexene, 0.785 g (0.00957 mol) of anhydrous sodium acetate, and 9 ml of acetic anhydride was heated at 110° for 4 hr. It was then diluted with 30 ml of water, stirred for 1.5 hr at room temperature, and extracted with ether. The ether extract was washed successively with water, 10% aqueous sodium carbonate, and water. It was dried and concentrated affording 0.689 g of a yellow oil. A 0.393-g sample of the crude product was distilled under vacuum through a short-path micro still (0.35 mm, pot temperature 50°). The first fraction was obtained as a colorless oil, 0.283 g, $n^{25}D$ 1.4646. A second fraction weighed 0.056 g (combined yield corrected for sample size distilled, 75%). An analytical sample was obtained by preparative glpc (5 ft × 0.25 in., 10% FFAP[45] on Chromosorb W).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.52; H, 8.02.

The nmr spectrum ($CDCl_3$) of **7a** showed the following absorptions: 1.40 to approximately 2.05 (m, 6 ring methylene protons), 2.05 (s, 6, $-O_2CCH_3$), 3.98 (s, 4, $-CH_2OAc$), 5.63 (broad s, 2, vinyl CH). The infrared spectrum ($CDCl_3$) of **7a** showed a strong band at 1730 cm^{-1} (ester C=O).

Acetolysis of 6-Oxabicyclo[3.2.1]octane-1-methyl *p*-Bromobenzenesulfonate.—The brosylate (17.5 g, 0.0485 mol), anhydrous sodium acetate (4.80 g, 0.0585 mol), and 455 ml of glacial acetic acid[46] were mixed in a round-bottom flask equipped with a condenser surmounted by a drying tube. The mixture was boiled under reflux for 369 hr. The mixture was cooled and the solution decanted from the precipitated sodium brosylate. To the solution were added, slowly, 238 g of sodium carbonate and 250 ml of water. This solution was subjected to manual and continuous ether extraction, affording 9.56 g of a yellow oil. This product mixture was redissolved in ether and washed with 10% aqueous sodium bicarbonate and water. It was dried and concentrated. Analysis of the reaction mixture by glpc using a 10% DEGS (diethylene glycol succinate) on Chromosorb W column (7 ft × 0.25 in.) with a column temperature of 158° and a flow rate of 46 cc/min revealed the presence of five compounds. The retention times in minutes measured from the air injection peak and percentages determined from ratios of integrated areas (shown in parentheses) are as follows: A, 11 (1.1); B, 13 (7.2); C, 17 (90.6); D, 34 (0.1); and E, 39 (0.9).

Glpc Collection of Acetolysis Products and Structural Characterizations.—The acetolysis products were collected using one or a combination of the following columns: 10% DEGS on Chromosorb W (7 ft × 0.25 in.), 20% DEGS on Chromosorb W (5 ft × 0.25 in.,), and 10% FFAP[44] (5 ft × 0.25 in.).

The nmr spectrum ($CDCl_3$) of compound A showed the following absorptions: 1.2–2.0 (broadened s, 8 ring methylene protons, 2.07 (s, 3, CH_3CO_2-), 2.33 and 2.41 (unsymmetrical[47] d, 2 ring methylene protons), 3.82 and 4.20 (AB d of d,[44] 2, J_{AB} = 8.5 Hz, $-OCH_2C<OAc$), 4.48 (broadened t, 1, C-5 H). The infrared spectrum of compound A ($CDCl_3$) showed strong bands at 1730 (ester C=O) and 1367 cm^{-1} (shoulder at 1377 cm^{-1}) (acetate CH_3). The mass spectrum (15 eV) of A shows a very weak molecular ion at *m/e* 184 and among the complex fragmentation ions an intense peak at *m/e* 124.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.08; H, 8.76. The structure assigned to A was **8** (see discussion under section titled Acetolyses).

The nmr spectrum of compound B showed the following absorptions: 1.15–2.00 (m, 10 ring methylene protons), 2.10 (s, 3, CH_3CO_2-), 4.02 and 4.18 (AB d of d,[40] 2, J_{AB} = 12 Hz, $-OCH_2C<OAc$), 4.47 (m, 1, C-5 H). The infrared spectrum of compound B ($CDCl_3$) showed a strong band at 1730 cm^{-1} (ester C=O) and a doublet at 1367 and 1387 cm^{-1} (acetate CH_3). The mass spectrum (15 eV) of B shows a molecular ion at *m/e* 184 and among the complex fragmentation ions an intense peak at *m/e* 124. The fragmentation patterns of A and B were quite similar.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.11; H, 8.71. The structure assigned to B was **9** (see discussion under section titled Acetolyses).

Compound C was identified as 1-acetoxymethyl-6-oxabicyclo-[3.2.1]octane (**6**) by comparison of its glpc retention time, nmr spectrum, and irspectrum with those of an authentic sample.

Compound E was identified as 4,4-bis(acetoxymethyl)-1-cyclohexene (**7a**) by comparison of its glpc retention time, nmr spectrum, and ir spectrum with those of an authentic sample.

Compound D could not be characterized because of insufficient sample size.

Acetolysis of 6-Oxabicyclo[3.2.1]octane-4-*d*-1-methyl *p*-Bromobenzenesulfonate.—The acetolysis was conducted as described for the acetolysis of the undeuterated brosylate starting with 2.46 g (0.00678 mol) of the deuterated analog **5b**. Using the same work-up procedure as previously described, 1.27 g of the solvolysis products were obtained as a yellow oil. Analysis of the reaction mixture by glpc using a 20% DEGS on Chromosorb W column (5 ft × 0.25 in.) with a column temperature of 162° and a flow rate of 46 cc/min revealed the presence of the five expected products. The retention times and relative percentages were as follows: A′, 13 (1.1); B′, 17 (6.7); C′, 20 (90.5); D′, 41 (0.2); and E′, 47 (1.4). The nmr spectrum ($CDCl_3$) of E′ (prime denotes deuterated analog) showed the following absorptions: 1.40 to approximately 2.05 (m, 6 ring methylene protons), 2.06 (s, 6, $-O_2CCH_3$), 3.99 (s, 4, $-CH_2OAc$), 5.63 (broadened s, approximately 1, vinyl CH). Careful comparisons of the integrated areas of this vinyl peak and the adjacent singlet at 3.99 indicated that E′ was approximately 45% monodeuterated. The intensities of the characteristic peaks in the mass spectrum (80 eV) at *m/e* 167 and 166 ($M^+ - CH_3CO_2H$) led to a value of 47% monodeuteration. The mass spectral analysis is probably accurate to within ±3%. The extent of deuteration determined above by nmr area integral comparisons is no better than ±5%.

Registry No.—**3**, 27025-13-4; **4a**, 21619-54-5; **4b**, 27025-15-6; **5a**, 27025-16-7; **5b**, 27025-17-8; **6**, 27025-18-9; **7a**, 27025-19-0; **8**, 27025-20-3; **9**, 27025-21-4.

(45) The abbreviation FFAP refers to "free fatty acid phase." It is a special reaction product from Carbowax 20M and 2-nitroterephthalic acid (see K. P. Dimrick, "G. C. Preparative Separations," Varian Aerograph, Palo Alto, Calif., 1966).

(46) Purified by treating with 1% by volume acetic anhydride and fractionally distilling.

(47) The higher field component of the "apparent doublet" is broadened through coupling of undetermined origin.