The Solvolytic Behavior of Some Sterically Compressed Systems

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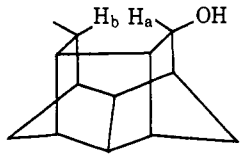
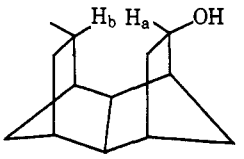
Abstract: The *p*-bromobenzenesulfonate derivatives of the epimeric alcohols I-OH and II-OH have been studied to determine how the unique steric compressions of this endo-endo fused bicycloheptane-type system affect solvolytic behavior. For comparative purposes the *p*-bromobenzenesulfonate derivatives of the corresponding epimeric alcohols from the noncompressed endo-exo fused system, III-OH and IV-OH, have also been studied. Two different solvent systems, acetic acid and pyridine, were used. With both solvent systems, ionizations *via* the norbornyl type bridged ion led to solvolysis products with exo solvent return on the noncompressed endo-exo fusion. However, with the *p*-bromobenzenesulfonate derivative of the endo alcohol II-OH some solvent-assisted reaction product was observed. In both solvents, elimination reactions occurred which gave the corresponding unrearranged olefins. Studies with deuterated derivatives of I-OH and III-OH indicated that these reactions are essentially exo-cis E2 eliminations and are independent of the ionization-based reactions. Rate studies have shown that for the sterically compressed systems, anchimerically assisted ionizations, solvent-assisted ionizations, and eliminations all show marked rate accelerations which are attributable to relief of the ground-state strain.

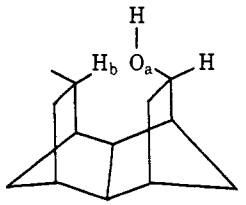
The half-cage system and the related endo,endo fused system of I-OH and II-OH, with their rigid geometries, present enormous steric oppositions between directly opposed inward facing groups such as H_a and H_b or OH_a and H_b. Such compressions in these systems have been found to give rise to abnormally high-frequency C–H stretching bands in the infrared[1] and also to unusually high shielding and deshielding effects in their nmr spectra.[2,3]



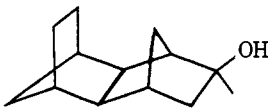
half-cage



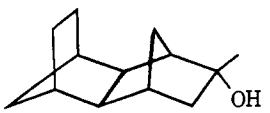
I-OH



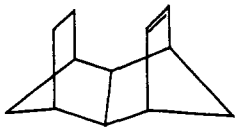
II-OH

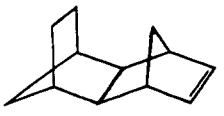


III-OH



IV-OH


olefin V


olefin VI

The endo,exo fused III-OH is related to I-OH *via* a Wagner–Meerwein rearrangement[4] but the inward facing groups are not directly opposed and are relatively free of steric opposition.[1] Consequently, a comparative study of the solvolytic behavior of derivatives of I-OH and III-OH together with their epimeric alcohols II-OH and IV-OH presents an opportunity to examine how this internal steric compression affects their chemistry.

Acetolysis Rates and Products

The acetolysis rates of the *p*-bromobenzenesulfonate derivatives of I-OH, II-OH, III-OH, and IV-OH are given in Table I together with the analysis of the products of reaction. A comparison of the rate of the sterically strained *exo*-norbornyl-type system I-OBs with that of the unstrained *exo*-norbornyl-type system III-OBs shows that the internal strain is causing a very marked rate acceleration (Table II).

This is attributable to relief of ground-state strain in moving from the I-OBs system to the solvolysis transition state which is presumed to have some of the less strained configuration of ion pair A. There are very many cases where relief of ground-state strain has been shown to have profound effects on the courses and rates of reactions.[5] However, this is a particularly large effect for a nonbonded strain interaction on the acetolysis rates of secondary alcohol sulfonates.[6]

As anticipated from previous work on the acetolysis of III-OBs,[4] both I-OBs and III-OBs give rise to the anchimerically assisted product III-OAc as the sole acetate. From both I-OBs and III-OBs significant amounts of olefin were formed. However, in each case only nonrearranged olefin was observed, *i.e.*, olefin V from I-OBs and olefin VI from III-OBs.

To gain further information on the nature of the elimination processes the exo monodeuterated compounds ID-OH and IIID-OH were prepared by deuterioboration-oxidation of the corresponding olefins.[7]

(1) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, **83**, 2938 (1961).
(2) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, **87**, 5247 (1965).
(3) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, **87**, 5249 (1965).
(4) L. de Vries and S. Winstein, *ibid.*, **82**, 5363 (1960).
(5) See, for example, H. C. Brown, *J. Chem. Soc.*, 1248 (1956).
(6) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964).
(7) Method of S. Wolfe, M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **22**, 1034 (1959), but with $LiAlD_4$ in place of $LiAlH_4$.

Table I. Acetolysis Rates and Reaction Products

ROBs[a]	Temp, °C	k, sec^{-1}	Acetolysis reaction products, mol % III-OBs	I-OAc	III-OAc	Olefin V	Olefin VI
I-OBs	25.02	$(1.04 \pm 0.03) \times 10^{-2}$	79		14	6.5	
ID-OBs	25.02	$(8.38 \pm 0.10) \times 10^{-3}$	83[c]		14[c]	3.3	
II-OBs	25.02	$(1.24 \pm 0.02) \times 10^{-5}$	28	10	60	1.4	
III-OBs	25.00	8.36×10^{-7}[b]					
III-OBs	75.00	$(5.53 \pm 0.08) \times 10^{-4}$[b]			97.7		2.3
IIID-OBs	75.00				99.1[c]		0.9
IV-OBs	25.00	3.76×10^{-8}[b]					
IV-OBs	75.00	$(3.54 \pm 0.05) \times 10^{-5}$[b]			99.6		0.4

[a] *Ca.* 0.010 *M* with 0.020 *M* NaOAc. [b] Rate constants from ref 4. [c] Monodeuterated.

Table II. Comparison of Acetolysis Rates at 25.0°

ROBs	k, sec^{-1}	Rel rate
I-OBs	1.04×10^{-2}	12,400
III-OBs	8.36×10^{-7}	1

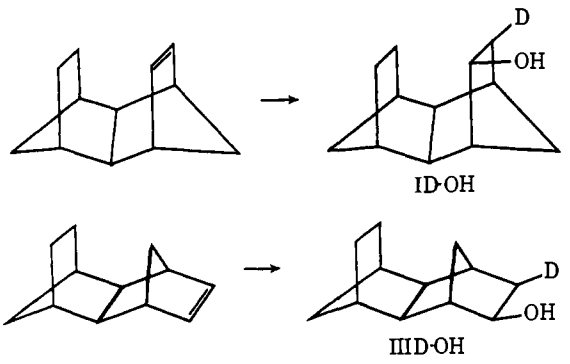
expected to increase steric strain in the initial stages and thereby be retarded. This problem has already been reported in previous work which showed that the acetolysis of the tosylate of II-OH is 22 times faster than *endo*-2-norbornyl tosylate.[8] The acceleration was

Table III. Acetolysis. Ionization and Elimination Rates

ROBs	Temp, °C	k_{obsd}, sec^{-1}	Fraction elimination	Calcd k_{ion}, sec^{-1}	Calcd k_{elim}, sec^{-1}
I-OBs	25.0	1.04×10^{-2}	0.065	9.8×10^{-3}	6.7×10^{-4}
ID-OBs	25.0	8.38×10^{-3}	0.033	8.1×10^{-3}	2.8×10^{-4}
III-OBs	25.0	8.36×10^{-7}	0.023[b]	8.2×10^{-7}	1.9×10^{-8}
III-OBs	75.0	5.53×10^{-4}	0.023	5.4×10^{-4}	1.2×10^{-5}
IIID-OBs	75.0	5.0×10^{-4}[a]	0.009	5.0×10^{-4}	4.5×10^{-6}

[a] Experimental data not available. This value is an estimate based on the rate constant for III-OBS. [b] Assumed to be the same as that observed at 75°.

From the acetolysis rates and product analysis data on I-OBs, ID-OBs, III-OBs, and IIID-OBs it is possible to make calculations of the individual rates for

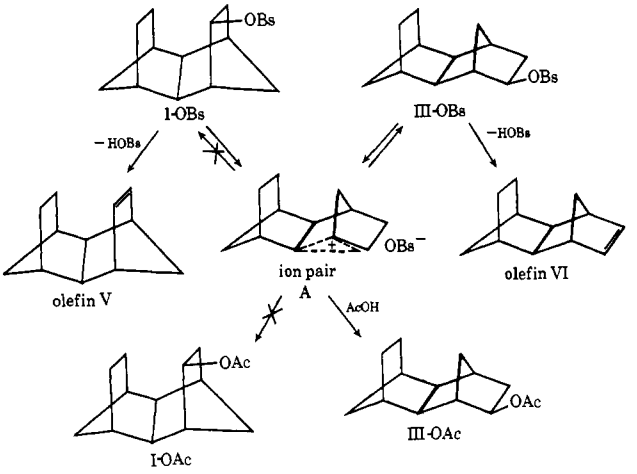


acetate formation (ionization) and for elimination (Table III). For I-OBs and ID-OBs these results indicate an isotope effect of 1.2 for ionization and 2.4 for elimination. For III-OBs and IIID-OBs with an assumed isotope effect for ionization of *ca.* 1.1, that for elimination is 2.7.

These are typical secondary isotope effects for the ionization processes but primary effects for the eliminations, and confirm that the two reactions have separate pathways.

A comparison of the calculated elimination rates of I-OBs and II-OBs at 25.0° (see Table III) shows that elimination from I-OBs is approximately 3.5×10^4 times faster. Again this is attributable to relief of ground-state strain in moving toward the unstrained olefin V system.

The acetolysis of II-OBs is particularly interesting in that the departure of the leaving group might be attributed to the very severe ground-state strain causing the leaving group to depart by a route other than perpendicular to the plane of the carbonium ion. The acceleration factor obtained by comparing the rates of II-OBs with IV-OBs is approximately 300 times.



The reason for the apparent difference in acceleration factors is that *endo*-2-norbornyl is a faster unstrained model than the IV-OBs system[9]

The acetolysis products from II-OBs show a very significant amount (10% molar) of I-OAc which presumably is derived from the anchimerically unassisted process (k_s); $k_{obsd} = k_s + k_\Delta$.[10]

(8) I. Rothberg, *Chem. Commun.*, 268 (1968).

(9) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, 74, 1127 (1952). Acetolysis of *endo*-2-norbornyl OBs at 25.0°, $k = 2.52 \times 10^{-6}$, *i.e.*, 7 times faster than IV-OBs.

(10) See, for example: (a) C. J. Lancelot and P. von R. Schleyer, *ibid.*, 91, 4297 (1969), and references cited therein; (b) A. F. Diaz and S. Winstein, *ibid.*, 91, 4302 (1969).

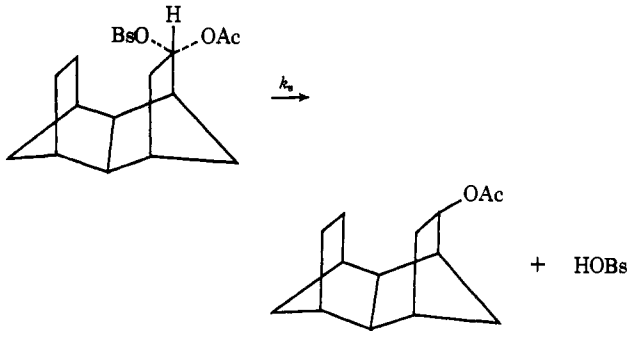
Table IV. Solvolysis in Pyridine. Rates and Reaction Products

ROBs[a]	Temp, °C	k, sec^{-1}	Reaction products, mol % III-OBs	III-salt	Olefin V	Olefin VI
I-OBs	25.00	$(1.10 \pm 0.04) \times 10^{-4}$			67	
I-OBs	50.20	$(1.51 \pm 0.04) \times 10^{-3}$	28	4–5	67	0
I-OBs	100.00[b]	*Ca.* 1.00×10^{-1}				
ID-OBs	25.00	$(6.8 \pm 0.15) \times 10^{-5}$			52	
ID-OBs	50.20	$(1.03 \pm 0.02) \times 10^{-3}$			49 + 2.5D	
III-OBs	100.03	$(2.77 \pm 0.05) \times 10^{-5}$	0	25[c]	0	75
IIID-OBs	100.03	$(1.39 \pm 0.05) \times 10^{-5}$				53.5 + 1.5D
IV-OBs	100.03	$(1.60 \pm 0.05) \times 10^{-5}$	0	90	0	10

[a] *Ca.* 0.010 *M*. [b] Extrapolated from the data at other temperatures. [c] Probably containing *ca.* 20% of the endo-substituted pyridinium salt.

Table V. Solvolysis in Pyridine. Ionization and Elimination Rates

ROBs	Temp, °C	k_{obsd}, sec^{-1}	Fraction elimination	Calcd k_{ion}, sec^{-1}	Calcd k_{elim}, sec^{-1}
I-OBs	50.2	1.51×10^{-3}	0.67	5.0×10^{-4}	1.01×10^{-3}
ID-OBs	50.2	1.03×10^{-3}	0.52	5.0×10^{-4}	5.3×10^{-4}
III-OBs	100.0	2.77×10^{-5}	0.75	6.9×10^{-6}	2.08×10^{-5}
IIID-OBs	100.0	1.39×10^{-5}	0.55	6.3×10^{-6}	7.6×10^{-5}



The acetolysis rate constant (k_{obsd}) for II-OBs at 25.0° = 1.24×10^{-5}. The molar fraction of I-OAc is 0.10 which indicates that $k_s = 1.2 \times 10^{-6}$. This is approximately 30 times greater than k_{obsd} for IV-OBs and shows that the anchimerically unassisted process must also be markedly accelerated by the steric strain.

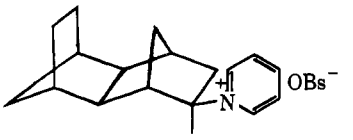
Solvolyses in Pyridine

Pyridine is a less ionizing solvent than acetic acid and generally gives rise to higher elimination fractions from these types of sulfonates. Consequently the behaviors of I-OBs, ID-OBs, III-OBs, IIID-OBs, and IV-OBs in anhydrous pyridine have been studied to gain further information on the nature of the elimination reactions.

In pyridine the sulfonates may undergo any of the alternative reactions: (a) isomerization (ion-pair return); (b) solvent substitution to give a quaternary pyridinium salt; (c) elimination to form olefin and sulfonic acid.

Reaction c yields acid which can be used to study the reaction rates by means of a simple titration (methanolic sodium methoxide solution and Thymol Blue indicator). Rate studies using this titration gave good first-order rate plots for single *p*-bromobenzenesulfonates.

The pyridinium salt isolated from the reaction products was assigned the structure III–salt, although there was evidence for some of the corresponding endo-pyridinium salt from III-OBs in pyridine. Deuterium analyses were carried out on the olefins obtained from ID-OBs and IIID-OBs. The rate constants and product analyses are summarized in Table IV.

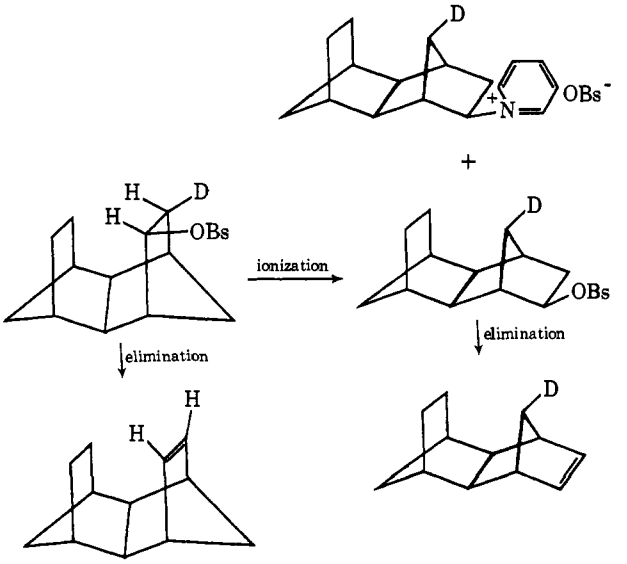


III–salt

The reaction rates show very similar trends to the acetolysis rate studies and a comparison of I-OBs and III-OBs again shows that the steric compression in I-OBs accelerates both the ionization and elimination fractions of the reaction to a very high degree.

Calculations of the individual rates for ionization and elimination of I-OBs, ID-OBs, III-OBs, and IIID-OBs are given in Table V. For the I-OBs system the isotope effects are 1.0 for ionization and 1.9 for elimination. The III-OBs system shows isotope effects of 1.1 and 2.7, respectively. These data confirm the general picture gained from the acetolysis studies.

The deuterium analyses on the olefin V from ID-OBs and also on olefin VI from IIID-OBs show very



low levels of residual deuterium and indicate that the eliminations are at least 95% exo-cis. A similar elimination with the III-OBs recovered from solvolysis of ID-OBs gave olefin VI which contained almost complete monodeuteration.

Elimination Mechanism

The elimination data from I-OBs, ID-OBs, III-OBs, and IIID-OBs in both solvent systems point to a very clean exo-cis E2 elimination. The vastly different reaction rates of I-OBs from its ion pair returned isomer III-OBs and the fact that any ion pair return gives only III-OBs make it easy to establish that no significant E1 elimination products occur, even though ionization processes are taking place simultaneously (*e.g.*, no olefin VI is obtained from I-OBs directly). The observed isotope effects for the eliminations ranged from 1.9 to 2.7 and are in line with previously reported values for E2 eliminations from *exo*-norbornyl systems.[11,12] Previous elimination studies of *exo*-norbornyl tosylate have shown the exo-cis elimination to be favored in strongly basic β elimination systems, selected to avoid the complications of simultaneous ionizations.[11-13]

Experimental Section

I-OH. Dihydroisodrin was dehalogenated to the endo,endo olefin V which was then converted to the alcohol by hydroboration–oxidation.[14] Recrystallization from ethanol gave needles, mp 108–109° (lit. 102°,[14] 108–109°[2]).

II-OH. A 4-g quantity of I-OH in 50 ml of ether was stirred vigorously with a solution of 16 g of chromic oxide in 75 ml of water for 2 hr at room temperature. The product was extracted from excess water with pentane. Evaporation of the pentane extract left a solid which was purified by elution with pentane from a neutralized, deactivated alumina column.[15] The product exhibited a double melting point, 69–70° and 90–91°,[2] in a yield of 2.5 g. Reduction of this ketone with lithium aluminum hydride in ether gave a product, mp 90–91°, after recrystallization from pentane: yield 1.8 g. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.96; H, 10.19.

III-OH and IV-OH. These alcohols were prepared by the methods of L. de Vries and S. Winstein.[4]

ID-OH. The monodeuterated alcohol was prepared by deuterioboration–oxidation of endo,endo olefin V. The technique used was essentially that of Sondheimer, *et al.*,[7] but lithium aluminum deuteride was used in place of lithium aluminum hydride. The alcohol, mp 108–109°, was obtained in 50% yield from the olefin. *Anal.* Calcd for $C_{12}H_{17}DO$: 5.55 atom % D. Found: 5.50 atom % D.

Endo,exo Olefin VI. A 4-g quantity of III-OBs was added to a solution of 8 g of freshly sublimed potassium *tert*-butoxide in 100 ml of dry benzene. After refluxing for 20 min, water was added and the product extracted with pentane. The product was purified by elution from a neutralized deactivated alumina column with pentane[15] and distilled, bp 100–103° (20 mm). The product obtained in a 1.1-g yield was shown to be a single component by vapor phase chromatography.[16]

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.83; H, 10.19.

IIID-OH. The monodeuterated alcohol was prepared by deuterioboration–oxidation of olefin VI using the same technique as was used for the preparation of ID-OH. The alcohol was obtained in a 55% yield from olefin, mp 123–124 (lit.[4] mp 123–124°).

Anal. Calcd for $C_{12}H_{17}DO$: 5.55 atom % D. Found: 5.46 atom % D.

***p*-Bromobenzenesulfonate Derivatives.** For alcohols II-OH, III-OH, IIID-OH, and IV-OH these derivatives were prepared by treating the appropriate alcohol with excess *p*-bromobenzenesulfonyl chloride in anhydrous pyridine using the method described by Winstein and Heck.[17]

However, the *p*-bromobenzenesulfonates of I-OH and ID-OH were too unstable for preparation by this method and a modified technique was developed. In a typical preparation 2.00 g of I-OH and 2.90 g of *p*-bromobenzenesulfonyl chloride (equimolar amounts) were dissolved in 10 ml of dry pyridine at −40° and maintained at this temperature for 24 hr. Pentane (100 ml) was added and the mixture shaken vigorously for approximately 1 min at room temperature. The pentane extract was quickly filtered and the solvent removed by evaporation under reduced pressure, the evaporation maintaining the temperature below 0°. Residual pyridine was removed in the same way under high vacuum. The residual solid was recrystallized from pentane at low temperature. The recrystallized solid was stored at −20° for periods of up to 1 week without significant decomposition or isomerization.

I-OBs was obtained in a yield of 60%: mp 67° dec; mp of resolidified material 85–88°; undepressed in mixture melting point with III-OBs.

Anal. Calcd for $C_{18}H_{21}O_3SBr$: C, 54.40; H, 5.32. Found: C, 54.50; H, 5.50.

ID-OBs. This monodeuterated compound was prepared from ID-OH by the same method as used for I-OBS and was obtained in similar yield: mp 67° dec.

II-OBs was obtained in a yield of 70%: mp 104–105°.

Anal. Calcd for $C_{18}H_{21}O_3SBr$: C, 54.40; H, 5.32. Found: C, 54.65; H, 5.63.

III-OBs was obtained in a yield of 70%: mp 90–91° (lit.[4] 90–91°).

IIID-OBs was obtained in a yield of 70%: mp 90–91°.

IV-OBs was obtained in a yield of 70%: mp 111–112° (lit.[4] 111–112°).

Acetolysis Products. All acetolysis product studies were on the reaction products from *ca.* 0.01 *M* solutions of the *p*-bromobenzenesulfonates in dry acetic acid containing 0.020 *M* sodium acetate. The reaction products were obtained by extraction with pentane from excess aqueous sodium bicarbonate solution. Qualitative and quantitative analyses of the olefin fractions were carried out by vpc analysis.[16] The individual acetates were not resolved by this method but it was impossible to estimate the individual olefin to total acetate ratio.

The acetate fractions from I-OBs, III-OBs, and IV-OBs were identified by ir spectra and saponification to give alcohol III-OH in each case. Quantitative information was obtained by studies of the nmr spectra of neat acetates. The proton α to the acetate group in III-OAc occurs at τ 3.96. The solvolysis acetates from I-OBs, III-OBs, and IV-OBs showed only this α proton band. Added amounts of I-OAc showed an additional α proton band at τ 5.03 and indicated that these solvolysis acetates contained less than 1% of I-OAc. By the same analysis method, the total solvolysis acetate from II-OBs was shown to contain 8–10% of I-OAc.

Examination of the reaction products from I-OBs and II-OBs after *ca.* 5 half-lives showed III-OBs to be present. This was obtained from a pentane extraction of the reaction product from aqueous sodium bicarbonate solution and identified by ir spectra, melting point, and mixture melting point. The proportions of III-OBs formed, indicated in Table I, were estimated from kinetic data.

Pyridine Solvolysis Products. I-OBs. A 2.0-g quantity of I-OBs in 150 ml of dry pyridine was maintained at 50° for 75 min. The reaction product was added to 500 ml of water and extracted with pentane. The pentane extract was washed with water, dilute sulfuric acid, water, dilute sodium bicarbonate solution, and again with water. Evaporation left a solid which, on recrystallization, gave 0.45 g of III-OBs, mp 88–89°, mixture melting point undepressed. The filtrate from the recrystallization was chromatographed on a column of neutralized deactivated alumina and elution with pentane gave a solid, mp 72–75°, which by ir and vpc[16] was shown to be a very pure form of olefin V.[14]

(11) H. C. Brown and K. T. Lin, *J. Amer. Chem. Soc.*, **92**, 200 (1970).
(12) N. A. Le Bel, *et al.*, *ibid.*, **85**, 3199 (1963); **86**, 4144 (1964).
(13) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).
(14) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).
(15) The olefins V and VI were somewhat volatile in pentane vapor and to avoid losses the solvent was removed by fractionation through a 12-in. Vigreux distillation column.
(16) A 2-m column based on pimelonitrile was used at a temperature in the 120–140° region. Typical retention times are olefin V, 2.0 min, olefin VI, 3.5 min, acetates, 40 min.
(17) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956).

The aqueous fraction from the pentane extraction was evaporated to dryness under reduced pressure to leave solid which on recrystallization from water yielded 0.46 g of needles, mp 186–187°.

Anal. Calcd for monohydrate $C_{23}H_{26}O_3NSBr \cdot H_2O$: C, 55.83; H, 5.75. Found: C, 55.75; H, 5.84.

III-OBs. A 1.0-g quantity of this compound in 100 ml of dry pyridine was heated in a sealed tube at 100° for 3 days. By the same techniques as those used for I-OBs products, olefin VI, pure by vpc analysis,[16] was obtained in 0.15-g yield and a pyridinium salt in a yield of 0.25 g, mp 175–185°. Studies of the nmr spectrum of the crude pyridinium salt from this reaction indicated that the endo:exo pyridinium ratio was *ca.* 4:1. (Nmr of $CDCl_3$ solutions showed purified salt to have a single proton peak at τ 5.38 attributable to the α proton to the pyridinium group. The crude salt showed a smaller second band at τ 4.84 which was attributed to the proton α to an endo-substituted pyridinium group.) Recrystallization of the crude salt gave a product, mp 186–187°, undepressed by the salt from I-OBs.

IV-OBs. By an identical procedure to that used for III-OBs, this product was found to yield pure olefin VI and pure salt, mp 186–187°, undepressed by the salt from I-OBs.

ID-OBs. By the procedure described for I-OBs, olefin V was obtained. A deuterium analysis showed that the olefin contained 0.49 atom % D. The isomerized III-OBs from this reaction was further solvolyzed in pyridine by the procedure described for III-OBs. The olefin VI obtained was compared with authentic olefin VI by ir spectral analysis. The spectra, taken on neat samples at 0.025-mm path length with a Beckman IR4 spectrophotometer, showed the spectrum of the isomerized material to contain a strong C–D stretch band at 2350 cm^{-1}. Bands at 998 and 747 cm^{-1}, present in the authentic sample spectrum, were completely absent.

IIID-OBs. This compound was treated by an identical procedure to that described for III-OBs. Olefin VI was obtained with a deuterium analysis of 0.34 atom % D.

Kinetics. For all of the *p*-bromobenzenesulfonates other than I-OBs and ID-OBs, acetolysis rate measurements were carried out in the normal manner using standard sodium acetate solution in acetic acid which was prepared as described previously.[18]

For acetolysis rates of I-OBs and ID-OBs a more rapid, *in situ* titration technique was used. The rates were followed by continuously titrating thermostated solutions of *ca.* 0.010 *M* sulfonate in dry acetic acid with a solution of 0.020 *M* sodium acetate in dry acetic acid using Bromophenol Blue indicator.

For the pyridine solvolysis studies, Karl Fischer grade pyridine was allowed to stand over Linde 4A molecular sieves powder for 24 hr and then redistilled. Standard sodium methoxide solution was prepared by adding sodium to redistilled methanol at about 0.4 g/l. and the resulting solution was standardized by titration against aqueous acid. The kinetic studies were carried out with 0.010 *M* solutions of the *p*-bromobenzenesulfonates, aliquots being sealed in ampoules and placed in thermostated baths. After suitable time intervals aliquots were titrated against the standard sodium methoxide solutions using Thymol Blue indicator. In all cases single *p*-bromobenzenesulfonates gave good first-order rate plots.

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A Dibenzohomotropylium Ion[1]

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Abstract: The 2,3;5,6-dibenzo-*cis*-4-hydroxybicyclo[5.1.0]octa-2,5-diene (**16**-OH) and the corresponding *trans*-4-hydroxy isomer **17**-OH were prepared by the reaction of $C_6H_5HgCBr_3$ with 2,3;5,6-dibenzotropone to give the dibromo ketone **14**. $NaBH_4$ reduction of **14** gave the cis 4-hydroxy compound which was debrominated by way of the tetrahydropyranyl ether with the aid of *n*-Bu_3SnH. Equilibration between **16**-OH and **17**-OH occurred in acidified aqueous dioxane. The corresponding 4-acetoxy, 4-methoxy, 4-keto, and 4-hydro compounds were prepared by conventional techniques. Stereochemical assignments were made by detailed examination of the nmr spectra of the cis and trans series of compounds. The dibenzohomotropylium cation **9**, which was prepared by protonation of **16**-OH in FSO_3H or H_2SO_4, showed considerable evidence for the heavy involvement of the cyclopropane protons in electron delocalization. Collapse of **9** with a nucleophile occurred predominantly upon the same face of the cation as the bridging methylene group, which is consistent with the observation that the cis acetate **16**-OAc solvolyzed some 10^2 times more rapidly than **17**-OAc. The kinetically controlled methanolysis product distribution of either acetate was the same, very largely **16**-OMe. Comparison is made of the solvolysis rates with other related systems and possible reasons for the observed stereoselectivity are discussed.

The concept of homoaromaticity, advanced[3] formally somewhat more than a decade ago, has found ample fulfillment in the many homoaromatic systems which have since been prepared and studied.[4] Such cyclic electron delocalization has frequently been observed with both cationic and anionic species but is much less important in neutral molecules.[4] The general concepts of homoaromaticity can be equally well applied to the transition states of pericyclic reactions[5] of both neutral molecules and ions.[4,6]

The monohomotropylium cation **1** was the first monohomoaromatic cation to be characterized. It was obtained in 1962 by Rosenberg, Mahler, and Pettit[7]

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