The Question of π-Electron Delocalization in the Bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl Cation. The Acetolysis of Bicyclo[2.2.1]hept-2-ene-*syn*- and -*anti*-7-methyl and Bicyclo[2.2.1]heptane-7-methyl *p*-Bromobenzenesulfonates[1]

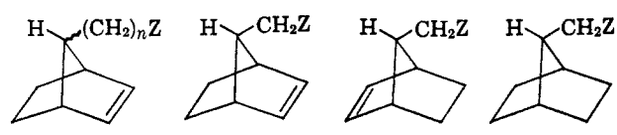
RUTA K. BLY AND ROBERT S. BLY

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received October 25, 1965

The acetolysis of bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl *p*-bromobenzenesulfonate is unaided by π-electron delocalization and exhibits considerable bimolecular character. At 115° it yields predominantly bicyclo[2.2.1]-hept-2-ene-*syn*-7-methyl acetate plus *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl acetate and a mixture of secondary acetates similar to those formed in the acetolyses of bicyclo[2.2.2]oct-5-en-*endo*-2-yl arenesulfonates. The acetolysis of bicyclo[2.2.1]hept-2-en-*anti*-7-methyl *p*-bromobenzenesulfonate also exhibits some bimolecular character and at 115° yields mostly bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl acetate, some *syn*-7-methylbicyclo-[2.2.1]hept-2-en-*anti*-7-yl acetate, and a mixture of secondary acetates similar to those formed in the acetolyses of bicyclo[2.2.2]oct-5-en-*exo*-2-yl arenesulfonates. Under similar conditions the acetolysis of bicyclo[2.2.1]-heptane-7-methyl *p*-bromobenzenesulfonate shows less bimolecular character than those of the unsaturated brosylates and yields bicyclo[2.2.1]heptane-7-methyl, 7-methylbicyclo[2.2.1]hept-7-yl, bicyclo[2.2.2]oct-2-yl, and bicyclo[3.2.1]oct-*exo*-2-yl acetates. At 130° the saturated brosylate is 2.35 times as reactive as the *syn* brosylate which is in turn 1.67 times more reactive than the *anti* brosylate. An explanation is offered to account for the nature and proportion of the products in each case.

Many examples of participation by π electrons of a nearby double bond in the rate-limiting step of a solvolysis reaction are known.[2] The effect is potentially greater when the double bond is highly strained,[3] when the leaving group departs a primary carbon,[4] when the double bond and the carbon carrying the leaving group are fixed in close proximity throughout the course of the reaction,[5] and when the developing positive charge is disposed symmetrically with respect to both ends of the double bond.[6] In an effort to determine the effect of overlap geometry upon the extent of such π-electron participation we have examined the solvolytic reactivity of the bicyclo[2.2.1]hept-2-ene-7-alkyl brosylates (**1**) where $n = 1$ and 2. This series of compounds fulfills most of the desired conditions and offers the additional advantage of a leaving group which is bonded to a carbon of "normal" hybridization.[7] We report here the syntheses and acetolyses of bicyclo[2.2.1]-hept-2-ene-*syn*- and -*anti*-7-methyl and bicyclo[2.2.1]-heptane-7-methyl *p*-bromobenzenesulfonates, **2b**, **3b**, and **4b**, respectively.



1 **2** **3** **4**

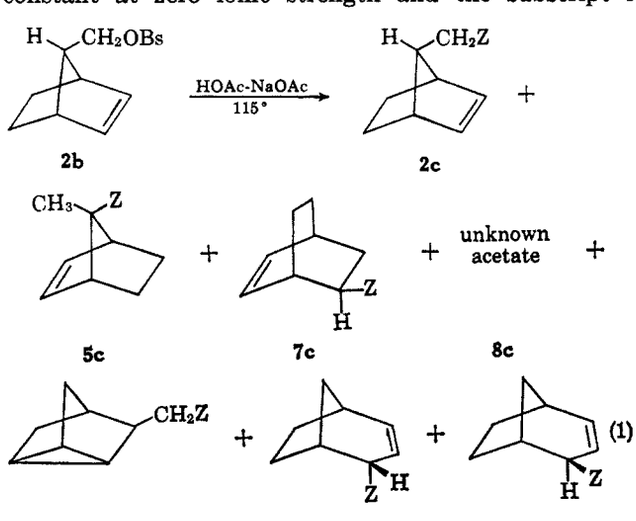
a, Z = OH **d**, Z = OTs
b, Z = OBs **e**, Z = NH_2
c, Z = OAc

Results

Kinetics.—The apparent first-order titrimetric rate constants, *k* (see Experimental Section), for the solvolysis of **2b**, **3b**, and **4b** in anhydrous acetic acid containing about 1% acetic anhydride are recorded in Table I. The dependence of the rate of each acetolysis upon added sodium acetate, sodium brosylate, and lithium perchlorate—expressed by the parameters b_n in the equation[8]

$$k = k_0(1 + b_1[\text{salt 1}]_i + b_2[\text{salt 2}]_i)$$

where k_0 is the apparent first-order titrimetric rate constant at zero ionic strength and the subscript i



a, Z = OH **d**, Z = OTs
b, Z = OBs **e**, Z = NH_2
c, Z = OAc

(1) A preliminary report of this work was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964; Abstracts, p 6C.

(2) For recent summaries, see (a) J. A. Berson in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 111 ff; (b) B. Capon, *Quart. Rev.* (London), **18**, 85 (1964).

(3) (a) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140 ff; (b) H. C. Brown and S. Nishida, Abstracts of the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 20; *cf.* (c) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (d) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960); (e) unpublished work of H. J. Schmid and K. C. Schreiber, reported by S. Winstein and M. Shatavsky, *ibid.*, **78**, 595 (1956).

(4) Provided that nucleophilic participation by the solvent is held to a minimum, *e.g.* (a) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953); (b) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); (c) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965).

(5) *Cf.* (a) R. G. Lawton, *ibid.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952); (d) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1288 (1965).

(6) (a) P. D. Bartlett and D. G. Sargent, *ibid.*, **87**, 1297 (1965); (b) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 590 (1960); (c) S. Winstein and R. L. Hansen, *Tetrahedron Letters*, **No. 25**, 4 (1960).

(7) (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); see also (b) R. C. Fort, Jr., and P. Schleyer, *Chem. Rev.*, **64**, 277 (1964), for a discussion of this point.

(8) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

TABLE I

APPARENT FIRST-ORDER RATE CONSTANTS FOR THE ACETOLYSIS OF THE BICYCLIC BROSYLATES

Run	Compd	Temp, °C	$[ROBs]_i$, M	$[NaOAc]_i$, M	μ_i	$10^5 k$, sec^{-1}
1	**2b**	99.4	0.0215	0.0299	0.0312	0.175
2			0.0216	0.0309	0.0322	0.195
3			0.0216	0.0296	0.0309	0.198
4		115.0	0.0212	0.0295	0.0313	0.873
5			0.0212	0.0290	0.0308	0.874
6		115.2	0.0412	0.0852	0.0906	1.29
7		129.7	0.0207	0.0295	0.0917[a]	4.29[a]
8			0.0208	0.0642	0.0947[b]	4.26[b]
9			0.0206	0.0876	0.0949	4.65
10			0.0425	0.0849	0.0920	4.57
11			0.0208	0.0558	0.0605	3.98
12			0.0209	0.0295	0.0320	3.30
13			0.0207	0.0292	0.0317	3.32
14	**3b**	99.4	0.0217	0.0300	0.0313	0.153
15			0.0216	0.0311	0.0324	0.156
16			0.0215	0.0297	0.0310	0.140
17		115.0	0.0204	0.0296	0.0315	0.638
18			0.0212	0.0295	0.0314	0.651
19		115.4	0.0430	0.0839	0.0893	0.971
20		129.7	0.0207	0.0295	0.0931[c]	3.16[c]
21			0.0209	0.0635	0.0936[d]	3.29[d]
22			0.0208	0.0851	0.0922	3.68
23			0.0435	0.0846	0.0917	3.54
24			0.0207	0.0556	0.0602	2.95
25			0.0207	0.0299	0.0324	2.35
26			0.0206	0.0294	0.0319	2.33
27	**4b**	99.4	0.0213	0.0300	0.0313	0.412
28			0.0214	0.0311	0.0324	0.410
29			0.0214	0.0302	0.0315	0.403
30		115.0	0.0209	0.0292	0.0310	1.82
31			0.0209	0.0293	0.0311	1.92
32		115.2	0.0371	0.0856	0.0910	2.51
33		129.7	0.0205	0.0296	0.0929[e]	10.88[e]
34			0.0208	0.0637	0.0940[f]	8.82[f]
35			0.0400	0.0858	0.0930	9.02
36			0.0204	0.0842	0.0912	9.03
37			0.0205	0.0560	0.0607	8.15
38			0.0205	0.0292	0.0317	7.28
39			0.0206	0.0293	0.0318	7.11
40			0.0226	0.0255	0.0276	7.00
41			0.0200	0.0251	0.0280	7.11

[a] Contains 0.0551 M lithium perchlorate. [b] Contains 0.0232 M sodium p-bromobenzenesulfonate. [c] Contains 0.0564 M lithium perchlorate. [d] Contains 0.0229 M sodium p-bromobenzenesulfonate. [e] Contains 0.0561 M lithium perchlorate. [f] Contains 0.0231 M sodium p-bromobenzenesulfonate.

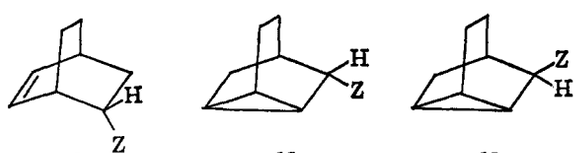
stands for initial concentration—are given in Table II. The derived activation parameters for the acetolysis of each brosylate (see Experimental Section) are listed in Table III.

TABLE II

DEPENDENCE OF APPARENT FIRST-ORDER ACETOLYSIS RATES AT 129.7° UPON ADDED SALTS

Compd	$10^5 k_0$, sec^{-1}	Value of b for added NaOAc	NaOBs	$LiClO_4$
2b	2.65	8.74	2.03	6.55
3b	1.59	15.2	4.54	9.54
4b	6.21	5.45	3.16	10.5

Products.—The acetolysis of bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl p-bromobenzenesulfonate (**2b**) at 115° (eq 1) yields a mixture which contains—in addition to a small amount of hydrocarbon(s)—the unrearranged acetate **2c**, *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl acetate (**5c**), tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**), bicyclo[3.2.1]oct-3-en-*endo*-2-yl acetate (**10c**), bicyclo[3.2.1]oct-3-en-*exo*-2-yl acetate (**11c**), bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**), an unidentified acetate **8c** (see Experimental Section), and at least four diacetates. The acetolysis mixture from **2b** contains no detectable amount (*i.e.*, more than ~0.1%) of bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl acetate (**3c**), tricyclo[2.2.2.$0^{2,6}$]oct-*endo*-3-yl acetate (**12c**), tricyclo[2.2.2.$0^{2,6}$]oct-*exo*-3-yl acetate (**13c**), or bicyclo[2.2.2]oct-5-en-*endo*-2-yl acetate (**6c**).[9] The relative proportion



6 **12** **13**

a, Z = OH
b, Z = OBs
c, Z = OAc
d, Z = OTs
e, Z = NH_2

of the various acetates in the acetolysis mixture, determined as described in the Experimental Section, is recorded in Table IV.

TABLE III

ACTIVATION PARAMETERS FOR THE ACETOLYSIS OF THE BICYCLIC BROSYLATES

Compd	ΔH^*, kcal/mole	ΔS^*, eu
Bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl OBs (**2b**)	27.0 ± 0.2	−12.6 ± 0.5
Bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl OBs (**3b**)	26.3 ± 0.2	−15.0 ± 0.5
Bicyclo[2.2.1]heptane-7-methyl OBs (**4b**)	27.4 ± 0.2	−10.1 ± 0.5

TABLE IV

COMPOSITION OF THE ACETOLYSIS MIXTURE OF BICYCLO[2.2.1]HEPT-2-ENE-*syn*-7-METHYL p-BROMOBENZENESULFONATE (**2b**) AT 115° IN BUFFERED ACETIC ACID

Compd[a]	% composition[b] at 0.42 half-life[c]	1.02 half-lives[d]	9.0 half-lives
5c	0.6 ± 0.2	0.6 ± 0.2	0.6 ± 0.2
2c	87.2 ± 1.0	86.5 ± 1.0	78.5 ± 1.0
7c	0.4 ± 0.2	0.5 ± 0.2	0.5 ± 0.2
8c	1.2 ± 0.3	1.2 ± 0.3	1.2 ± 0.3
9c	<0.1	~0.2	0.8 ± 0.4
10c	3.0 ± 0.5	3.0 ± 0.5	2.8 ± 0.5
11c	7.5 ± 0.5	7.5 ± 0.5	7.6 ± 0.5
Diacetates	...	~0.5	8.0 ± 0.5

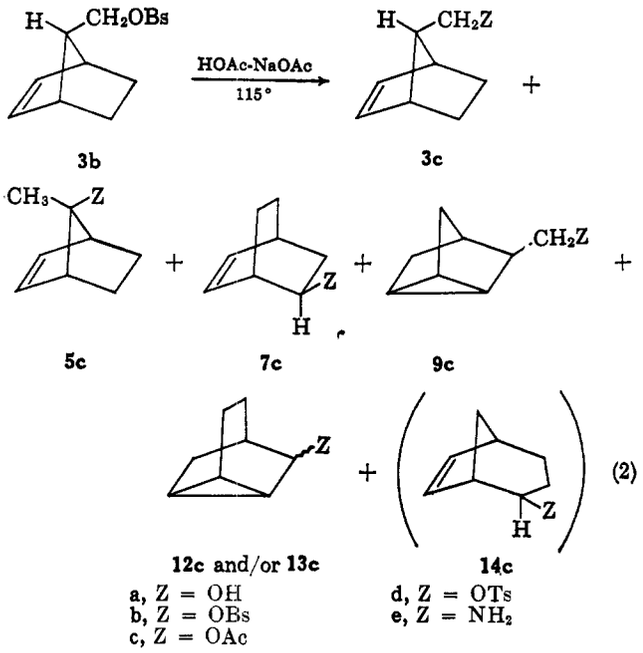
[a] In order of elution from the 20-ft Carbowax column. [b] Excluding hydrocarbon(s). [c] 79% of the starting brosylate, **2b**, uncontaminated with isomeric brosylates, was recoverd from the reaction mixture. [d] 48% of the starting brosylate, **2b**, uncontaminated with isomeric brosylates, was recovered from this reaction mixture.

All of the mixtures from the acetolysis of bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl p-bromobenzenesulfonate (**3b**) at 115° (eq 2) contain—in addition to small amounts of unidentified hydrocarbon(s)—unrearranged acetate **3c**, tertiary acetate **5c**, bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**), tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**), one or both of the two tricyclo-

(9) Berson and Gajewski,[10] who have solvolyzed **2b** in buffered acetic acid at 120° and analyzed the products by capillary gas chromatography, apparently find, in addition to **2c**, **5c**, **7c**, **9c**, **10c**, **11c**, and some diacetates, small amounts of **6c**, **12c**, **13c**, and **14c**.

(10) J. A. Berson and J. J. Gajewski, *J. Am. Chem. Soc.*, **86**, 5020 (1964).

[2.2.2.0^{2,6}]oct-3-yl acetates (**12c** and **13c**), and appreciable amounts of at least four diacetates. The acetolysis mixture after ten half-lives also contains a small amount of an ester which we have tentatively identified as bicyclo[3.2.1]oct-6-en-*exo*-2-yl acetate (**14c**) by comparison of its retention time and that of



its reduction product with authentic samples. None of the acetolysis mixtures from **3b** contain appreciable amounts of bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl acetate (**2c**), bicyclo[2.2.2]oct-5-en-*endo*-2-yl acetate (**6c**), or bicyclo[3.2.1]oct-3-en-*endo*- or *-exo*-2-yl acetates (**10c** and **11c**, respectively).[11] The relative proportion of the acetates present in the acetolysis mixtures at various reaction times is recorded in Table V.

TABLE V

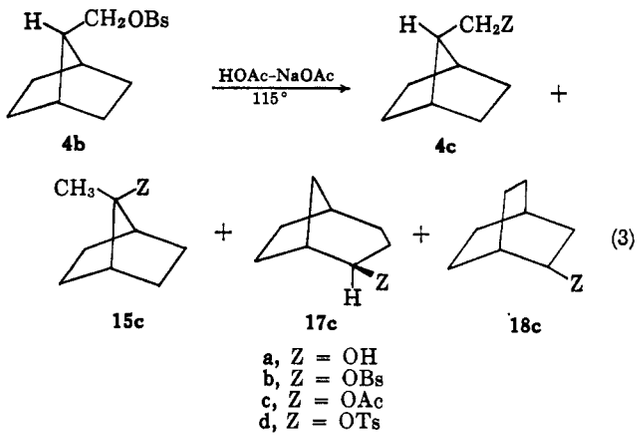
COMPOSITION OF THE ACETOLYSIS MIXTURE OF BICYCLO-[2.2.1]HEPT-2-ENE-*anti*-7-METHYL *p*-BROMOBENZENESULFONATE (**3b**) AT 115° IN BUFFERED ACETIC ACID

	% composition[b] at		
Compd[a]	0.44 half-life[c]	1.02 half-lives[d]	10 half-lives
5c	5.5 ± 0.5	5.5 ± 0.5	5.5 ± 0.5
3c	92 ± 2	87 ± 2	30 ± 2
7c	0.5 ± 0.3	1.1 ± 0.3	1.7 ± 0.3
9c	...	~0.1	2.5 ± 0.5
14c	...	...	~0.3
12c and/or **13c**	1.0 ± 0.5	~0.3	...
Diacetates	1 ± 0.5	6 ± 1	60 ± 2

[a] Table IV, footnote *a*. [b] Table IV, footnote *b*. [c] 78% of the starting brosylate, **3b**, uncontaminated with isomeric brosylates, was recovered from this reaction mixture. [d] 48% of the starting brosylate, **3b**, uncontaminated with isomeric brosylates, was recovered from this reaction mixture.

The acetolysis of bicyclo[2.2.1]heptane-7-methyl *p*-bromobenzenesulfonate (**4b**) at 115° (eq 3) yields—in addition to traces of hydrocarbon(s)—unrearranged acetate **4c**, 7-methylbicyclo[2.2.1]hept-7-yl acetate (**15c**), bicyclo[3.2.1]oct-*exo*-2-yl acetate (**17c**), and bicyclo[2.2.2]oct-2-yl acetate (**18c**). We were unable to

(11) Berson and Gajewski[10] apparently find both of the tricyclic acetates **12c** and **13c** and "undetectably small amounts" of **10c** and **6c** in addition to the products which we have detected in the acetolysis mixture of **3b**.



detect any bicyclo[3.2.1]oct-*endo*-2-yl acetate (**16c**) in the acetolysis mixtures. The product composition at various reaction times is shown in Table VI.

TABLE VI

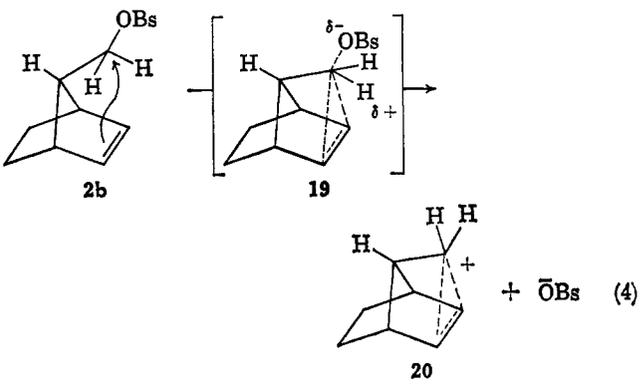
COMPOSITION OF THE ACETOLYSIS MIXTURE OF BICYCLO-[2.2.1]HEPTANE-7-METHYL *p*-BROMOBENZENESULFONATE (**4b**) AT 115° IN BUFFERED ACETIC ACID

	% composition[b] at	
Compd[a]	0.48 half-life[c]	10 half-lives
14c	3.0 ± 0.5	3.0 ± 0.5
4c	62.0 ± 1.0	62.0 ± 1.0
17c	15.5 ± 1.0	15.5 ± 1.0
18c	19.5 ± 1.0	19.5 ± 1.0

[a] Table IV, footnote *a*. [b] Table IV, footnote *b*. [c] 70% of the starting brosylate, **4b**, uncontaminated by isomeric brosylates, was recovered from this reaction mixture.

Discussion

π-Electron Participation in the Rate-Limiting Step.—Symmetric π-electron delocalization could conceivably



enhance the unimolecular ionization of **2b**, *viz.*, eq 4, but not that of **3b** or **4b**. Thus, a plot of log k_1 *vs.* σ^* (where k_1 is the true unimolecular acetolysis constant of RCH_2OBs and σ^* is the Taft inductive substituent parameter of R) for these latter two brosylates can be used (in conjunction with the appropriate σ^*) to estimate the true unimolecular acetolysis constant of **2b** in the absence of π-electron participation.[12] The necessary σ^* values, calculated from the pK_a values of the bicyclic acids **21**, **22**, and **23** (see Experimental Section),[12a] are recorded in Table VII. Because these

(12) (a) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 641; (b) A. Streitwieser, *J. Am. Chem. Soc.*, **78**, 4935 (1956).

TABLE VII
DATA FOR THE TAFT–STREITWIESER PLOTS

R	Acetolysis of RCH_2OBs at 129.7°: $10^5\ k_1^{min}$, sec^{-1}	Acetolysis of RCH_2OBs at 129.7°: $10^5\ k_1^{max}$, sec^{-1}	pK_a of RCOOH in H_2O at 25°	σ^*
Bicyclo[2.2.1]hept-2-en-*syn*-7-yl	0.42 ± 0.04[a]	2.69 ± 0.14[b]	4.66 ± 0.02	−0.006 ± 0.012
Bicyclo[2.2.1]hept-2-en-*anti*-7-yl	0.16 ± 0.05[a]	1.59 ± 0.04[b]	4.50 ± 0.01	+0.087 ± 0.007
Bicyclo[2.2.1]hept-7-yl	2.7 ± 0.1[a]	6.25 ± 0.08[b]	4.85 ± 0.01	−0.116 ± 0.008

[a] Based upon the acetate ratios at 115°; *cf.* Tables IV–VI. [b] Table II.

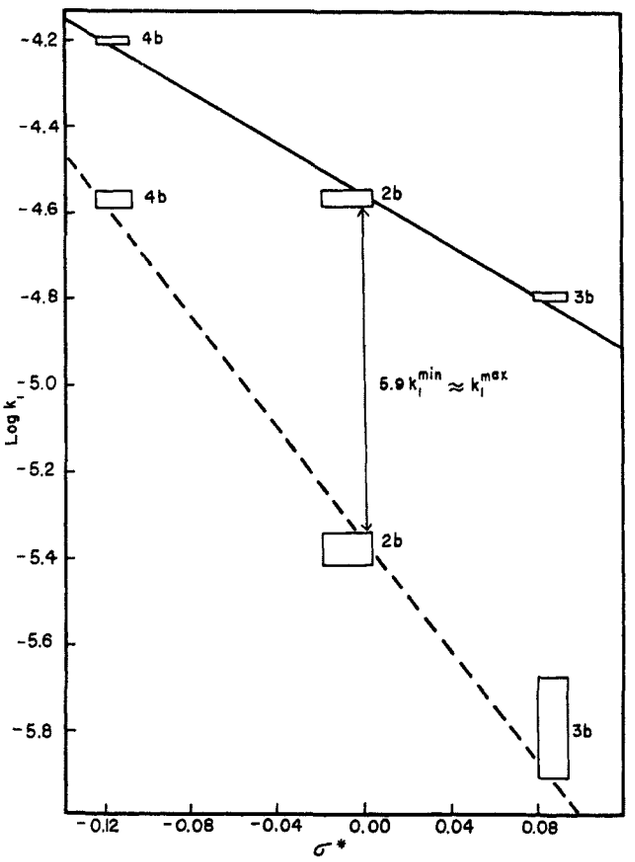
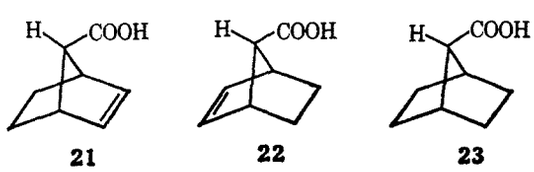


Figure 1.—Plot of the Taft substituent constant, σ^*, of R *vs.* the logarithm of the estimated minimum (———) and maximum (———) first-order acetolysis constants of RCH_2OBs at 129.7° (Table VII).

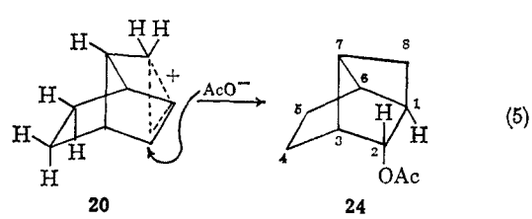
acetolyses exhibit considerable bimolecular character,[13] the exact values of k_1 for **2b**, **3b**, and **4b** are not known.



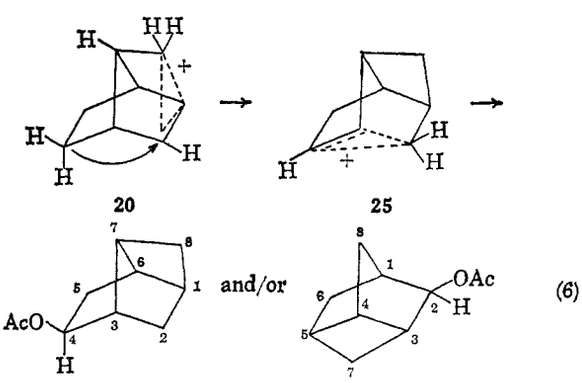
21 **22** **23**

However, the true k_1 values may not be *greater* than the apparent first-order titrimetric constants at zero ionic strength, *i.e.*, $k_1^{max} \leq k_0$, nor *less* than the total rate constants for the formation of secondary and tertiary acetates, *e.g.*, $k_1^{min} \geq k$(% *sec*-OAc + % *t*-OAc)/100. These maximum and minimum values of k_1 for **3b** and **4b** (Table VII) can be used (in place of the actual k_1 values) to estimate similar limits for the *unassisted* k_1 of **2b**. It is apparent from the log k_1 *vs.* σ^* plots[12] (Figure 1) that the true k_1 of **2b** exceeds its estimated unassisted k_1 by not more than six times, and probably by considerably less than that amount.[14] Hence, either the π-electrons of the *syn* isomers act to increase the ΔF for ionization of **21** by the same amount that they decrease ΔF^* for the unimolecular acetolysis of **2b**, or they do not significantly aid the latter reaction by delocalization in the rate-limiting step.

π-Electron Participation in the Product-Determining Steps.—If the symmetric, delocalized carbonium ion **20** were formed as a discrete intermediate at any stage during the acetolysis of **2b**, one might expect to find some tricyclo[4.2.0.$0^{3,7}$]oct-*anti*-2-yl acetate (**24**) among the products, *i.e.*, eq 5.[16] Alternatively, since the formation of **24** would require **20** to react with acetate at a sterically hindered position, it might undergo an internal hydride shift and yield tricyclo[4.2.0.$0^{3,7}$]oct-*exo*-4-yl acetate (**26**) and/or tricyclo[3.2.1.$0^{3,6}$]oct-*exo*-2-yl acetate (**27**) *via* the asymmetric delocalized cation **25** (eq 6).[17] With the possible exception of **8c**, we find no evidence for the presence of any unidentified tricyclic acetates in the mixtures from the acetolysis of **2b**, even though we suspect that such tricyclic products would



20 **24** (5)



20 **25** **26** **27** (6)

(13) As evidenced by the relatively large effect of added sodium acetate (Table II) upon their acetolysis rates—Fainberg and Winstein[8] have observed *b* values of 1.1, 3.3, and 10.0, respectively, for lithium acetate, lithium tosylate, and lithium perchlorate in the typically unimolecular acetolysis of neophyl *p*-bromobenzenesulfonate at 75°—and the relatively high proportion of primary acetates in their acetolysis products (Tables IV–VI).

(14) The reaction parameter, $\rho^* = -2.95$, calculated from the slope of the estimated maximum k_1 values, is about what might be expected for the acetolysis of a hindered primary derivative,[12b,15] while that calculated from the estimated minimum k_1 values, *viz.*, $\rho^* = -6.40$, is considerably more negative than those reported for other solvolytic reactions.[12b]

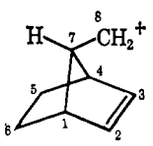
(15) H. Felkin and G. Le Ny, *Bull. Soc. Chim. France*, 1169 (1957).

(16) *Cf.* G. Le Ny, *Compt. Rend.*, **251**, 1526 (1960).

(17) *E.g.*, the acetolysis of β-(bicyclo[2.2.1]hept-2-en-*syn*-7-yl)ethyl *p*-bromobenzenesulfonate yields a mixture of tricyclo[4.3.0.$0^{3,7}$]non-*exo*-4-yl and tricyclo[4.2.1.$0^{3,7}$]non-*endo*-2-yl acetates: R. K. Bly, R. S. Bly, A. O. Bedenbaugh, and O. R. Vail, Abstracts of the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 25P.

have survived the reaction conditions had they been formed.[18]

In summary, *it appears that the acetolysis of* **2b** *derives little or no assistance from* π*-electron delocalization in the rate-limiting step and that less than 1% of the total products of the reaction could result from a symmetric* π*-electron delocalized carbonium ion intermediate.* We attribute this lack of π-electron delocalization to the fact that in the undeformed primary carbonium ion **28**, the C_2–C_8 and C_3–C_8 distances are too large, *viz.*, 2.8 A,[19] to permit effective $\pi\pi$-type overlap of the π-orbital at C_2 and C_3 with the vacant p orbital at C_8[21] while effective $\sigma\sigma$-type overlap is precluded by the unfavorable geometry of the system.[19]



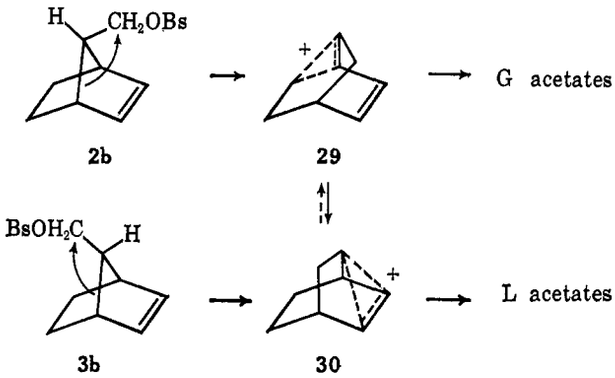
28

The Nature of the Unimolecular Acetolyses.—Our data do not permit a unique description of the course of the unimolecular acetolysis of **2b, 3b,** or **4b.** However, certain deductions can be made and we suggest that the following best accommodate the experimental facts as we now know them.

As Berson and Gajewski have pointed out,[10] the secondary acetates produced in the solvolyses of **2b** and **3b** fall into two categories, those that have been identified by LeBel (L) as products of the acetolysis of bicyclo[2.2.2]oct-5-en-*exo*-2-yl *p*-bromobenzene- or *p*-toluenesulfonate, **7b** or **7d**,[22] *viz.*, bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**), tricyclo[2.2.2.$0^{2,6}$]oct-*endo*-3-yl acetate (**12c**), and bicyclo[3.2.1]oct-6-en-*exo*-2-yl acetate (**14c**)—the L series,[10] and those which Goering[23] (G) has reported as acetolysis products of bicyclo[2.2.2]oct-5-en-*endo*-2-yl *p*-toluenesulfonate, **6d**, *viz.*, bicyclo[2.2.2]oct-5-en-*endo*-2-yl acetate (**6c**) and bicyclo[3.2.1]oct-3-en-*endo*- and -*exo*-2-yl acetates (**10c** and **11c**, respectively)—the G series.[10] The nature of the secondary acetates in each case is determined by the fact that solvolysis of **2b** or **3b** with ring enlargement gives the G (**29**) or the L (**30**) intermediate, respectively (Scheme I).

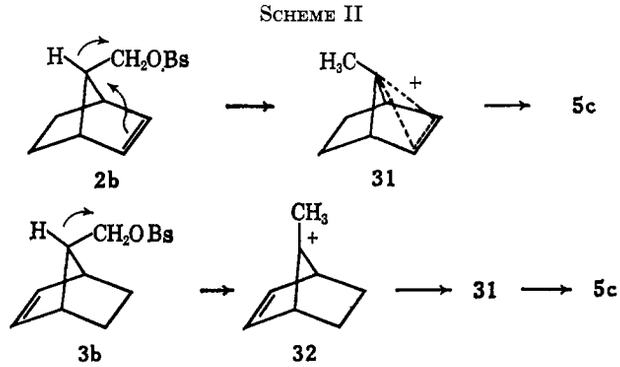
The *syn* brosylate **2b** yields a mixture of L and G acetates with the latter predominating by a factor of 20–40 times (Table IV),[9] while the *anti* brosylate **3b**—as far as we have been able to detect[11]—yields only L acetates (Table V). This suggests that the G or L intermediate, whichever is formed first, reacts preferentially with the nucleophile rather than "twitch" to the other conformation.[10]

SCHEME I



The same tertiary acetate (**5c**) is formed from the acetolysis of each unsaturated brosylate. This is the result of a hydride migration which yields the charge-delocalized cation (**31**) in each case (Scheme II).

SCHEME II



The data in Tables IV and V indicate that the *syn* brosylate **2b** yields 20 times more secondary acetate (**7c**, **10c**, and **11c**) than tertiary (**5c**), while the *anti* brosylate **3b** yields 5.3 times more tertiary acetate (**5c**) than secondary (**7c**, **12c**, and/or **13c**). We believe that these preferences for ring enlargement and hydride migration, respectively, are conformationally determined.[24] The *syn* brosylate (**2b**), in the absence of π-electron participation, solvolyses predominately from the more stable staggered conformation (**33**)[26] which makes for facile ring enlargement. The *anti* brosylate **3b**, because of nonbonded interactions between the geminal hydrogens at C_8 and the *exo* hydrogens at C_5 and C_6 which render the staggered conformation less

(18) *Cf.* (a) R. A. Parent, Ph.D. Dissertation, Rutgers University, 1963; (b) R. R. Sauers and R. A. Parent, Abstracts of the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 7C; (c) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

(19) Calculated using the method of E. J. Corey and R. A. Sneen [*J. Am. Chem. Soc.*, **77**, 2505 (1955)], the norbornene geometry of Roberts, *et al.*,[20] and an assumed C_7–C_8 distance of 1.525 A.

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

(21) H. J. Kopineck, *Z. Naturforsch.*, **5A**, 420 (1950).

(22) N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

(23) (a) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961); (b) H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(24) If the initial ionization in each case were to result in a conformationally mobile primary carbonium ion which reacted further by either ring enlargement or hydride migration, the *anti* brosylate **3b** should produce the larger ratio of secondary-to-tertiary acetate because the LeBel intermediate (**30**) is more stable[25] and intervenes earlier in the course of ring enlargement of the *anti* ion (**35**) than does the Goering intermediate (**29**) in the ring enlargement of the *syn* ion (**28**), and because π-electron participation should enhance the migratory aptitude of the hydrogen in the *syn* ion (**28**) with respect to that in the *anti* (**35**).

(25) It can be calculated that at 25° **7d** would be about 40 times as reactive as **6d**.[22,23]

(26) There is evidence, based upon its inability to form an intramolecular hydrogen bond,[27] that bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) adopts a conformation in dilute solution which directs the hydroxyl group away from the π electrons of the double bond.

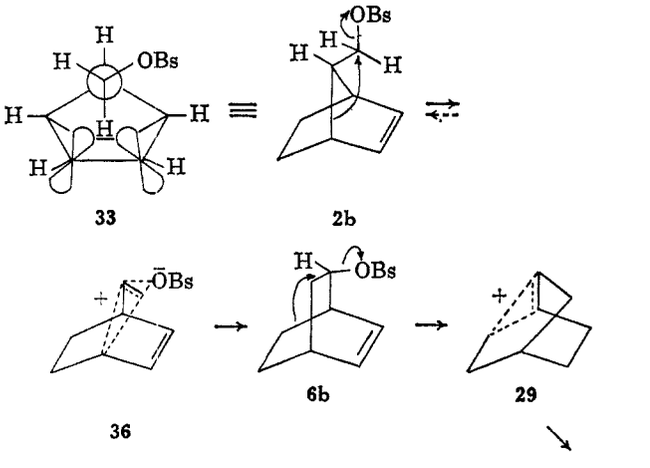
(27) Unpublished work of L. P. Kuhn, R. S. Bly, R. E. Bowman, and R. K. Bly; *cf.* 9th Annual Report on Research under the sponsorship of the Petroleum Research Fund, 1964, p 38.

stable,[28] solvolyses instead from the near-eclipsed form (**34**).[30]

Added salts (Table II) have a uniformly greater effect upon the acetolysis rate of the *anti* brosylate. This indicates that its ionization is accompanied by greater charge separation in the transition state of the rate-limiting step than is that of the *syn* brosylate.[31] We picture the initial intermediate in the *anti* case as a charge-localized ion pair (**35**) and that in the *syn* as a charge-delocalized ion pair (**36**) to accommodate this observation.

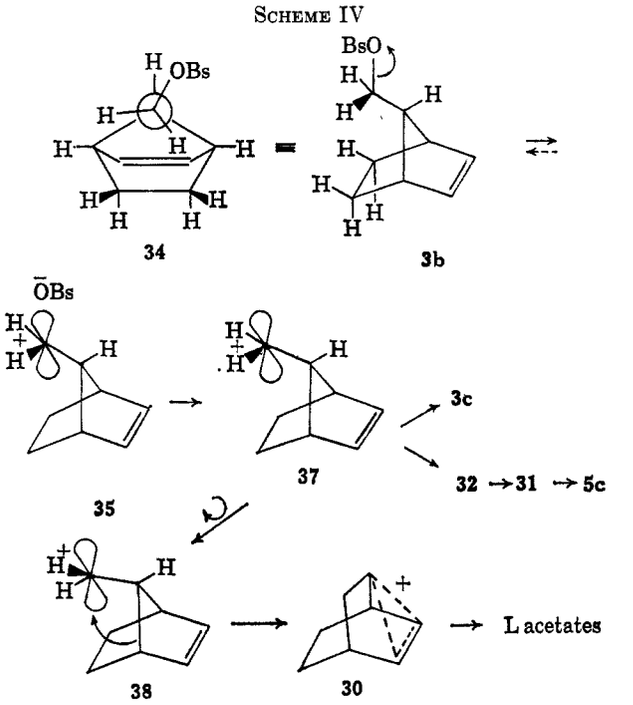
Combining these deductions, we suggest that the predominant course of unimolecular acetolysis for the *syn* brosylate **2b** is that depicted in Scheme III, *i.e.*,

SCHEME III



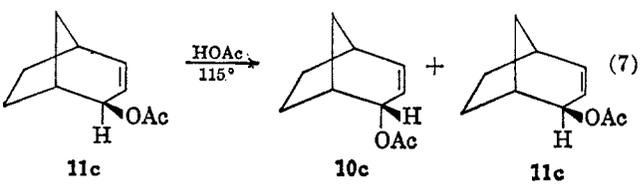
ionization from a staggered conformation (**33**) directly to the charge-delocalized ion pair (**36**) which returns either to starting material or to bicyclo[2.2.2]oct-5-en-*endo*-2-yl *p*-bromobenzenesulfonate (**6b**). The ring-enlarged brosylate **6b**—undetectable kinetically because it is much more reactive than **2b**[32]—upon further acetolysis yields the G acetates *via* the Goering intermediate (**29**). We picture (Scheme IV) the unimolecular acetolysis of the *anti* brosylate **3b** as occurring predominately from the near-eclipsed conformation (**34**) to yield the ion pair **35** which either returns to starting brosylate or dissociates to **37**. The free cation (**37**) then either yields primary acetate **3c** by direct nucleophilic attack, undergoes hydride migration to yield **32** and thence tertiary acetate **5c**, or rotates about the C_7–C_8

SCHEME IV

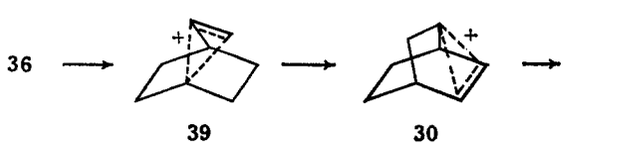


bond to give **38** which produces the LeBel intermediate (**30**) by ring enlargement.

Goering reports that at 30° the acetolysis of **6d** yields 98.6% **11c**, 0.5% **10c**, 0.4% **6c**, and 0.5% of an unidentified acetate.[23] We find that the allylic acetate **11c** epimerizes in acetic acid at 115° to a 70:30 mixture of **11c**:**10c** (eq 7). Thus, the only G acetates which we



have been able to detect in the mixture from the acetolysis of the *syn* brosylate **2b** at 115° are **10c** and **11c**. Even though bicyclo[2.2.2]oct-5-en-*endo*-2-yl acetate (**6c**) is stable under our reaction conditions, we would not have detected it unless it had constituted a considerably larger proportion of the G acetates in this case than it does in the acetolysis of **6d**. Since bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**) is formed neither in the acetolysis of **6d** at 25° nor in the acetolysis of bicyclo[3.2.1]oct-3-en-*exo*-2-yl acetate (**11c**) at 115°, the small amount of **7c** which we observe in the acetolysis products of **2b** must arise from a crossover to the LeBel intermediate which occurs before the Goering intermediate has been fully developed. A likely path is the dissociation of the charge-delocalized ion pair, *viz.*, eq 8.



LeBel has found that the acetolysis of bicyclo[2.2.2]-oct-5-en-*exo*-2-yl *p*-bromobenzenesulfonate (**7b**) at 25°

(28) If one assumes models in which the angle strain is always a minimum, then the staggered conformation of **3b** places each geminal hydrogen at C_8 within ~2.3 A of an *exo* hydrogen at C_5 or C_6 while the near-eclipsed conformation **34** places the *endo* C_8 hydrogen within ~2.0 A of both of the *exo* hydrogens at C_5 and C_6, and the "*exo*" C_8 hydrogen in an eclipsed position with respect to the hydrogen at C_7. Conversion of the staggered to the near-eclipsed conformation, if it were to occur purely by rotation about the C_7–C_8 bond, would require one of the C_8 hydrogens to pass within ~1.8 A of one of the *exo* hydrogens at C_5 or C_6. The van der Waals radius of hydrogen is ~1.2 A.[29]

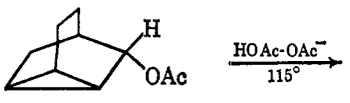
(29) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1940, p 189.

(30) The near-eclipsed conformation **3b** is the only one from which ionization of the brosylate would lead to a decrease in nonbonded interaction in the transition state.

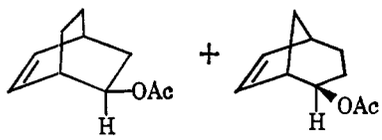
(31) *Cf.* (a) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961); (b) S. Winstein and J. Sonneberg, *ibid.*, **83**, 3235 (1961).

(32) It can be calculated that **6b** would be about 36 × 10^4 times as reactive as **2b** at 25°.[23]

yields a mixture containing 81% tricyclo[2.2.2.$0^{2,6}$]oct-*endo*-3-yl acetate (**12c**), 17% bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**), and 2% bicyclo[3.2.1]oct-6-en-*exo*-2-yl acetate (**14c**).[22] We find, however, that **12c** is not stable at 115° but is converted instead to a mixture of **7c** (84%) and **14c** (16%) (eq 9), *i.e.*, 5.3:1 **7c**:**14c**.



12c

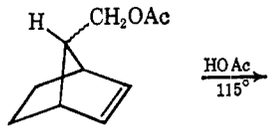


7c **14c** (9)

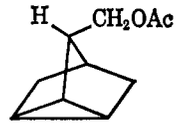
Since crossover from G to L occurs only to the extent of ~0.5% in the acetolysis of the *syn* brosylate **2b** at 115°,[33] the total amount of **14c** formed in this crossover would be 0.5 × 0.16 = 0.08%, too small for us to have detected. In the acetolysis of the *anti* brosylate **3b**, however, where the secondary acetates are entirely L and constitute about 2% of the total reaction product after ten half-lives,[33] we find only **7c** and **14c** in the expected ratio of ~5.7 ± 0.5 to 1.

The relatively small amount of tertiary acetate **5c** that is formed during the acetolysis of **2b** could arise from a competitive hydride migration (Scheme II) or from rearrangement of the charge-delocalized ion **39**.

The total amount of primary acetates plus diacetates remains constant throughout each reaction, *viz.*, **2c** + **9c** + diacetates ≈87% (Table IV); **3c** + **9c** + diacetates ≈93% (Table V). Thus it seems likely that in each case both the tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**) and the diacetates are formed from the unrearranged primary acetates, **2c** or **3c**, respectively (eq 10). The greater reactivity of the *anti* acetate **3c** is in accord with the *exo* approach of acetic acid to the double bond.



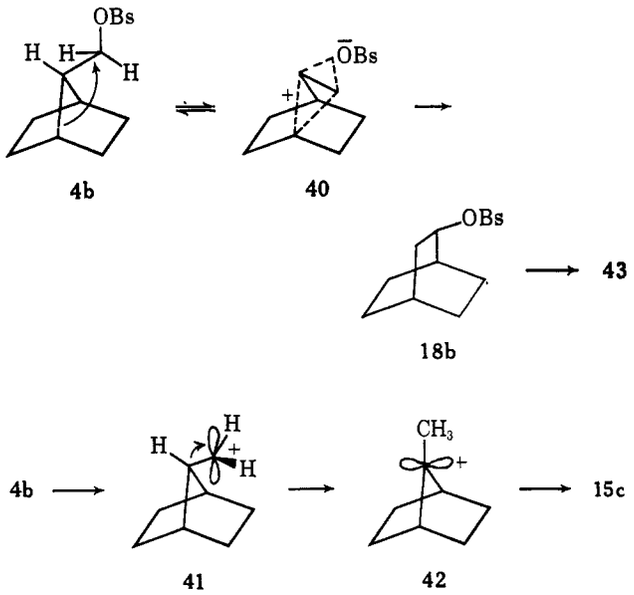
2c or **3c**



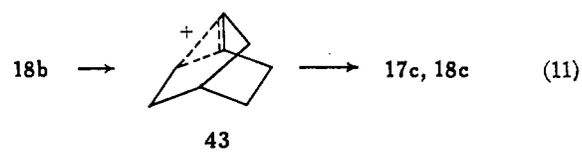
9c + diacetates (10)

The acetolysis of bicyclo[2.2.1]heptane-7-methyl *p*-bromobenzenesulfonate (**4b**) is somewhat more facile than those of the unsaturated brosylates (Tables I–III) and—judging from the lower *b* value for added sodium acetate (Table II) and the relatively smaller proportion of primary acetate (**4c**) in the product mixture (Table VI)—occurs with less concomitant bimolecular displacement. These effects must be the result of a lower field-induced retardation[35] to unimolecular ionization in the saturated compound (Figure 1). The relatively high ratio of secondary:tertiary acetate in the product, *viz.*, 12:1 (Table VI), may be due to preferential return of brosylate ion to bicyclo[2.2.2]oct-2-yl *p*-bromobenzenesulfonate (**18b**)[37] from a charge-delocalized ion pair such as **40** and/or to the reluctance of the primary ion **41** to undergo a C_7–C_8 hydride shift to form the relatively unstable 7-methylbicyclo-[2.2.1]heptyl cation **42** (Scheme V).

SCHEME V



The ratio of **18c** to **17c** in the acetolysis of **4b**, *i.e.*, 1.2:1, is similar to that observed in the solvolysis of **17b** and **18b** at 25° (1.3:1),[23,38] in the acetolysis of β-(cyclohex-3-en-1-yl)ethyl *p*-bromobenzenesulfonate at 25° (1.2:1),[39] and to the ratio of **18a**:**17a** (1.1:1) formed in the nitrosative deamination of bicyclo[2.2.1]-heptane-*exo*-2-methylamine at 25°.[40] It seems likely that the same charge-delocalized ion (**43**) is the product-determining intermediate for the secondary acetates in all these cases, *viz.*, eq 11.



(11)

(33) The greater extent of crossover that is observed in each case when the corresponding bicyclo[2.2.1]hept-2-ene-*syn*- and -*anti*-methylamines, **2e** and **3e**, are subjected to nitrosative deamination[10] must simply reflect the fact that the resulting "hot" cationic intermediates[34] are in vibrationally excited states and hence more "twitchy."

(34) A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957).

(35) We use the term "field-induced retardation" to distinguish between the retardation arising from a molecular dipole at the center of mass which, because of its orientation, coulombically opposes the developing C→O dipole, *i.e.*, a "field effect,"[36] and a retardation which results when a highly electronegative center induces a hybridizational change in a neighboring atom—by deforming their common σ orbital—which is transmitted through the σ bonds, from atom to atom, between the electronegative center and the developing C→O dipole, *i.e.*, an "inductive effect."[36] Since this inductive effect is not normally transmitted through more than about three bonds, we assume that it is negligible in the case of these bicyclic brosylates.

(36) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 280–285.

(37) Kinetically indetectable since **18b** is considerably more reactive than **4b**; *cf* ref 23.

(38) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3214 (1963).

(39) (a) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961); (b) H. L. Goering and G. N. Fickes, Abstracts of the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 6Q.

(40) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

Experimental Section[41]

Bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (2a).—A slurry of 0.97 g (0.024 mole) of 95% lithium aluminum hydride in 75 ml of anhydrous ether was cooled to 0°, and 2.65 g (0.0199 mole) of granular, anhydrous aluminum trichloride was added in small portions. The mixture was stirred at room temperature for 1 hr, then cooled to $-25 \pm 5°$. While this temperature was maintained, a solution of 4.73 g (0.387 mole) of spiro[bicyclo-[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane][42] in 100 ml of ether was added dropwise over a 1-hr period. The reaction mixture was allowed to warm to 10°, stirred at this temperature for 10 min, and then recooled to −25°. An aqueous, 15% sodium hydroxide solution (10 ml) was cautiously added with vigorous stirring. The mixture was warmed to room temperature and the precipitated inorganic salts were removed by filtration. The filtrate was dried over anhydrous potassium carbonate and the solvent was removed by distillation at atmospheric pressure.

A gas–liquid partition chromatographic analysis of the residue on the silicone oil[41] column at 135° indicated the presence of one major component (80%, relative retention time 1), two minor components (17% total, relative retention times 0.77 and 0.88, respectively), and about 3% total of several other impurities.

The product mixture was chromatographed on a 1.5 × 25 cm column packed with 100 g of Merck acid-washed alumina. The column was eluted successively with 150 ml of pentane, 100 ml of a 9:1 pentane–ether mixture, and 300 ml of ether. The eluate was collected in 20-ml fractions and each fraction was analyzed by glpc as before. Most of the contaminants were eluted with the pentane in fractions 3–5. The desired alcohol (**2a**) was eluted with the ether in fractions 14–23.

The alcohol-containing fractions were combined and dried over anhydrous sodium sulfate. The solvent was distilled at atmospheric pressure and the residue was distilled under vacuum to yield 2.51 g (52.2%) of product, bp 74–77° (5 mm). The spectral and analytical data of this alcohol have been reported previously.[42]

Bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl *p*-Bromobenzenesulfonate (2b).[43]—To an ice-cold solution of 2.41 g (0.0194 mole) of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) in 25 ml of anhydrous pyridine was added, in three portions, 5.31 g (0.0208 mole) of *p*-bromobenzenesulfonyl chloride. The mixture was swirled at ice-bath temperature for 10 min to dissolve the sulfonyl chloride and then allowed to stand overnight in a refrigerator at ~5°. The solution was poured into 150 ml of ice–water and the precipitated product was separated by suction filtration. A recrystallization from hexane gave 5.16 g (77.5%) of white crystals: mp 88–91°; ν_{max}^{KBr} 3095, 3070, 1630, 707 (–HC=CH–), 1370, and 1280 cm^{-1} (–OSO$_2$–); nmr, $\nu_{max}^{CCl_4}$ τ 2.33 (singlet, (4 =C*H*—, aromatic), 4.22 (unsymmetrical quintet, 2 =C*H*—, nonaromatic), 6.10 (doublet, J = 8 cps, 2 –O–CH_2CH<), 7.30 (poorly resolved quartet, 2 ⩾C–*H*, bridgehead), and 7.8–9.2 (complex multiplet, 1 ⩾C$_7$–*H*, 2 >C*H*H, and 2 >CH*H*).

Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.99; H, 4.41; Br, 23.28; O, 13.98. Found: C, 49.04; H, 4.55; Br, 23.39; O, 13.96.

This material was used for the acetolysis studies without further purification.

Bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl Acetate (2c).—A solution of 50 mg (0.40 mmole) of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) and 0.5 ml of acetic anhydride in 1.0 ml of pyridine was heated under reflux for 12 hr. The reaction mixture was cooled to 10°, acidified to pH ~5, and extracted with four 5-ml portions of pentane. The combined pentane extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed by distillation through a 0.5 × 15 cm wire-spiral-packed column. The residue was distilled in a short-path still at 5 mm, using an oil-bath temperature of 115°, to give 51 mg (77%) of product: $\nu_{max}^{CCl_4}$ 3070, 1620, 716 (–HC=CH–), 1740, and 1234 cm^{-1} (–O–COCH$_3$); nmr, $\nu_{max}^{CCl_4}$ τ 4.16 (quintet, 2 =C*H*—),[42,44] 6.13 (doublet, J = 7 cps, 2 –O–CH_2CH<), 7.30 (broad sextet, 2 ⩾C–*H*, bridgehead), and 8.09 (singlet, 3 –COCH_3) superimposed on a multiplet at τ 8.0–9.2 (1 ⩾C$_7$–*H*, 2 >C*H*H, 2 >CH*H*).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.40; H, 8.66.

Bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl *p*-Bromobenzenesulfonate (3b).—This compound was prepared in the same manner as the *syn* isomer **2b**,[43] using 4.02 g (0.0324 mole) of bicyclo-[2.2.1]hept-2-ene-*anti*-7-methanol (**3a**),[42] 8.86 g (0.0347 mole) of *p*-bromobenzenesulfonyl chloride, and 40 ml of pyridine. The yield was 8.86 g (79.6%): mp 83–84°; ν_{max}^{KBr} 3090, 3060, 1640, 700 (–HC=CH–), 1360, and 1280 cm^{-1} (–OSO$_2$–); nmr, $\nu_{max}^{CCl_4}$ τ 2.32 (singlet, 4 =C*H*—, aromatic), 3.99 (triplet, J = 2.3 cps, 2 =C*H*—, nonaromatic),[42,44] 6.29 (doublet, J = 8 cps, 2 –O–CH_2CH<), 7.37 (poorly resolved sextet, 2 ⩾C–*H*, bridgehead), and 7.9–9.2 (complex multiplet, 1 ⩾C$_7$–*H*, 2 >C*H*H, and 2 >CH*H*).

Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.99; H, 4.41; Br, 23.28. Found: C, 49.18; H, 4.33; Br, 23.34.

This material was used for the acetolysis studies without further purification.

Bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl Acetate (3c).—This compound was prepared in the same manner as **2c**, using 11 mg (0.089 mmole) of bicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (**3a**), 0.5 ml of acetic anhydride, and 1 ml of pyridine. The yield was 8.0 mg (55%): $\nu_{max}^{CCl_4}$ 3070, 1610, 700 (–HC=CH–), 1750, and 1242 cm^{-1} (–O–COCH$_3$); nmr, $\nu_{max}^{CCl_4}$ τ 3.96 (triplet, J = 2 cps, 2 =C*H*—),[42,44] 6.38 (doublet, J = 8 cps, 2 –O–CH_2CH<), 7.36 (broad sextet, 2 ⩾C–*H*, bridgehead), 8.05 (singlet, 3 –COCH_3), and 8.1–9.2 (multiplet, 1 ⩾C$_7$–*H*, 2 >C*H*H, and 2 >CH*H*).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.23; H, 8.60.

Bicyclo[2.2.1]heptane-7-methanol (4a).—To a solution of 1.00 g (8.06 mmoles) of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) in 15 ml of absolute methanol was added 200 mg of 5% palladium-on-charcoal catalyst. The solution was stirred in an atmosphere of hydrogen until no more gas was taken up. The methanol was removed by distillation at atmospheric pressure and the product was distilled under vacuum in a short-path still (oil-bath temperature, 90–100°, pressure, 7 mm) to yield 0.99 g (97%) of the saturated alcohol **4a**: $\nu_{max}^{CCl_4}$ 3640 (O–H, nonbonded) and 3350 cm^{-1} (broad, O–H, bonded); nmr, $\nu_{max}^{CCl_4}$ τ 6.52 (doublet, J = 8 cps, 2 –O–CH_2CH<), 7.0 (singlet, concentration dependent, 1 O*H*), 7.92 (poorly resolved sextet, 2 ⩾C–*H*, bridgehead), and 8.0–9.1 (multiplet, 9 hydrogens).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.95; H, 11.13.

Bicyclo[2.2.1]hepane-7-methyl *p*-Bromobenzenesulfonate (4b).—This compound was prepared in the same manner as **2b**,[43] using 1.88 g (0.0149 mole) of bicyclo[2.2.1]heptane-7-methanol (**4a**), 4.17 g (0.0163 mole) of *p*-bromobenzenesulfonyl chloride, and 20 ml of pyridine. The yield was 3.98 g (77.5%): mp 90–93°; ν_{max}^{KBr} 1360 and 1280 cm^{-1} (–OSO$_2$–); nmr, $\nu_{max}^{CCl_4}$ τ 2.31 (singlet, 4 =C*H*—, aromatic), 6.09 (doublet, J = 8 cps, 2 –O–CH_2CH<), 7.92 (broad, 2 ⩾C–*H*, bridgehead), and 8.0–9.0 (complex multiplet, 9 hydrogens).

Anal. Calcd for $C_{14}H_{17}BrO_3S$: C, 48.70; H, 4.96; Br, 23.15. Found: C, 48.78; H, 4.93; Br, 23.16.

This material was used for the acetolysis studies without further purification.

Bicyclo[2.2.1]heptane-7-methyl Acetate (4c).—This compound was prepared in the same manner as the acetate **2c**, using 30 mg (0.24 mmole) of bicyclo[2.2.1]heptane-7-methanol (**4a**), 0.5 ml of acetic anhydride, and 1 ml of pyridine. The reaction yielded 31 mg (77%) of pure **4c**: $\nu_{max}^{CCl_4}$ 1745 and 1245 (broad, –O–COCH$_3$) cm^{-1}; nmr, $\nu_{max}^{CCl_4}$ τ 6.05 (doublet, J = 7.5 cps, 2 –O–CH_2CH<), 7.94 (broad 2 ⩾C–*H*, bridgehead), and 8.02 (singlet, 3–CO CH_3) superimposed over a multiplet at τ 8.0–9.1 (9 hydrogens).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.22; H, 9.70.

(41) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalitisches Laboratorium, Mülheim, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nmr spectra on a Varian A-60 spectrometer at ~35° using tetramethylsilane (τ 10.00) and/or chloroform (τ 2.69) as internal standards in carbon tetrachloride. The gas chromatographic analyses were carried out on an F and M Model 500 linear temperature-programmed gas chromatograph using helium as a carrier gas at flow rates of 50–120 cc/min. The chromatographic columns used were 0.25 in. × 8 ft coiled copper tubes packed with 20% Carbowax 20M on 100–140 mesh Gas-Chrom-S (Applied Science Laboratories, Inc., State College, Pa.) or 20% Silicone Oil 200 on 60–80 mesh Chromasorb P (Johns-Manville Products Corp.); a 0.25 in. × 7.5 ft coiled copper tube packed with 20% Carbowax 20M on 60–80 mesh Chromasorb W; and a 0.25 in. × 20 ft coiled copper tube packed with 20% Carbowax 20M on 100–140 mesh Gas-Chrom-S.

(42) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

(43) R. S. Tipson, *ibid.*, **9**, 235 (1944).

(44) *Cf.* E. J. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

***syn*-7-Methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl Acetate (5c).**—This material was prepared in the same manner as **2c**, using 500 mg (4.03 mmoles) of *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**5a**),[42] 1.5 ml of acetic anhydride, and 4 ml of pyridine. The yield of distilled material was 559 mg (83.6%): $\nu_{max}^{CCl_4}$ 3070, 1635, 719 (-HC=CH-), 1740, and 1246 cm^{-1} (-O-COCH$_3$); nmr, $\nu_{max}^{CCl_4}$ τ4.03 (triplet, J = 2 cps, 2 =CH-),[42,44] 7.12 (broad quintet, 2 >C-H, bridgehead), 8.09 (singlet, 3 -COCH$_3$), 8.16 (singlet, 3 >C-CH$_3$), and 8.0–8.5 (multiplet, 4 hydrogens).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.81; H, 8.25.

Tricyclo[2.2.1.0^{2,6}]heptane-3-methyl Acetate (9c).—This compound was prepared in the same manner as **2c**, using 180 mg (1.45 mmoles) of tricyclo[2.2.1.0^{2,6}]heptane-3-methanol (**9a**),[18] 1 ml of acetic anhydride, and 2 ml of pyridine. The acetate was isolated by collection from the 8-ft silicone oil column[41] at 150°. The yield was 169 mg (70.2%): $\nu_{max}^{CCl_4}$ 3070 (>C-H, nortricyclyl), 1745, and 1243 cm^{-1} (broad, -O-COCH$_3$); nmr, $\nu_{max}^{CCl_4}$ τ 6.25 (doublet, J = 7.5 cps, 2 -O-CH$_2$CH<) and 8.02 (singlet, 3 -COCH$_3$) superimposed on a multiplet at τ 8.0–9.1 (9 hydrogens).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.90; H, 8.29.

7-Methylbicyclo[2.2.1]hept-7-yl Acetate (15c).—To a solution of 220 mg (1.32 mmoles) of *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl acetate (**5c**) in 5 ml of absolute methanol was added 50 mg of 5% palladium-on-charcoal catalyst. The suspension was stirred under a hydrogen atmosphere until no more gas was taken up. The solvent was removed by distillation at atmospheric pressure. The residue was distilled in a short-path still at 5 mm pressure and an oil-bath temperature of 115° to give 150 mg (67.5%) of the saturated acetate **15c**. A gas chromatographic analysis of this material on the 20-ft Carbowax column[41] showed it to be homogeneous.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.13; H, 9.44.

Infrared absorptions were at $\nu_{max}^{CCl_4}$ 1740 and 1240 cm^{-1} (-O-COCH$_3$); nmr, $\nu_{max}^{CCl_4}$ τ 7.79 (quintet, 2 >C-H, bridgehead), 8.10 (singlet, 3 -COCH$_3$), 8.58 (singlet, 3 >C-CH$_3$), and 8.0–9.0 (multiplet, 8 hydrogens).

Bicyclo[3.2.1]octan-*exo*-2-ol (17a).—A 240-mg (1.45-mmole) sample of bicyclo[3.2.1]oct-3-en-*exo*-2-yl acetate (**11c**)[23] in 10 ml of methanol was stirred in a hydrogen atmosphere with 50 mg of 5% palladium-on-charcoal catalyst until no more hydrogen was absorbed. The catalyst was removed by filtration, 0.5 g of potassium hydroxide and 2 ml of water were added, and the solution was heated under reflux for 90 min. The cooled alkaline solution was diluted to 30 ml with water and extracted with 30 ml of pentane on a continuous extractor for 36 hr. The pentane extract was washed with 10 ml of water and dried over anhydrous sodium sulfate. The pentane was removed by distillation at atmospheric pressure through a short Vigreux column, and the residue sublimed to give 119 mg (65.1%) of pure alcohol **17c**, identical in all respects with an authentic sample.[23]

Acetolysis Rates.—The titrimetric acetolysis rates were determined on ~0.02 M solutions of the alkyl brosylate in anhydrous acetic acid containing ~0.03 M sodium acetate and ~1% acetic anhydride as described previously.[45] The solutions were protected from moisture at all times. The apparent titrimetric first-order acetolysis rate constant, k, was computed for each run from the slope of the line which results when the logarithm of the fraction of unreacted brosylate at time t is plotted against t (Table I). Since acetic acid adds rapidly to a strained double bond such as that in **2b** and **3b**, it is necessary to carry out these rate determinations in the presence of excess sodium acetate as a buffer. Hence, the apparent first-order rate constants obtained in this manner must actually represent both the unimolecular and bimolecular portions of the reaction, *viz.*

$$k \approx k_1 + k_2[AcO^-] + k_3[AcOH]$$

where k is the apparent first-order titrimetric rate constant, k_1 is the true first-order titrimetric rate constant, k_2 is the true bimolecular rate constant for displacement by acetate ion, and k_3 is the true bimolecular rate constant for displacement by un-ionized acetic acid. When our data are treated in this fashion, the resulting plots show no appreciable deviation from linearity to about 70% reaction.[46] The experimental infinity titers at ~10 half-lives are consistently within 3% of the calculated values. By determining k at the same temperature for several different initial acetate ion concentrations, $[AcO^-]_i$, and extrapolating a plot of k *vs.* $[AcO^-]_i$ to $[AcO^-]_i = 0$, a value of the apparent first-order titrimetric rate constant at zero initial ionic strength, k_0 (Table II), can be obtained where

$$k_0 \approx k_1 \approx k_3[AcOH]$$

Rather than determine k_0 at more than one temperature, we have calculated the activation parameters in the Eyring equation from values of k determined for runs at similar initial acetate ion concentrations (*viz.*, runs 2–5, 12–18, 25–31, 38, and 39, Table I). Values of ΔH^* and ΔS^* obtained in this manner are recorded in Table III.

Acetolysis Products.—The acetolysis mixture from each of the bicyclic brosylates at 115° was analyzed at a concentration similar to those used for the kinetic runs, *cf.*, runs 4, 17, and 30 (Table I). Products were determined at more than one reaction time in each case. In a typical determination, a 0.023 M solution of the brosylate **2b** in anhydrous acetic acid containing 0.033 M sodium acetate and ~1% acetic anhydride was thermostated in a sealed tube at 115° for 0.42 half-life, cooled, diluted with ice–water, and filtered (gravity) to remove unreacted brosylate. The recovered brosylate was dried, weighed (79% of starting material was recovered), and shown by comparison of its infrared and nmr spectra with those of an authentic sample to be identical within experimental error (±5%) with the starting brosylate. The aqueous filtrate was extracted exhaustively with small portions of pentane; the combined pentane extract was washed with saturated sodium chloride and sodium bicarbonate solutions, dried over anhydrous sodium sulfate, and concentrated by distillation of most of the solvent through a 0.5 × 15 cm wire-spiral-packed column. A portion of the concentrate was analyzed by gas chromatography for hydrocarbons, mono-, and diacetates on the temperature-programmed (125 to 200° at a constant 2.9°/min) 7.5-ft Carbowax column[41] using an initial helium flow of 100 cc/min, and for monoacetates isothermally at 175° on the 20-ft Carbowax column[41] using a helium flow of 80 cc/min. Since all of the products could not be resolved by gas chromatography of the acetates, a portion of the concentrate was reduced with an ethereal suspension of lithium aluminum hydride. The excess hydride was hydrolyzed with 15% aqueous sodium hydroxide; the supernatant ethereal solution was decanted, dried over anhydrous sodium sulfate, and analyzed isothermally at 145° on the 8-ft Carbowax column.[41] The per cent composition reported for the original acetolysis mixture in each case (Tables IV–VI) is a composite of the integrated and normalized (exclusive of solvent) peak areas from the chromatograms of the acetates and those of the alcohols. No correction has been made for differences in thermal conductivity. The analytical results are reproducible.

The individual acetates and alcohols were isolated where feasible by preparative gas chromatography, on the 20-ft Carbowax column[41] at 175°, from distilled portions of each acetolysis and reduced acetolysis mixture. The collected materials were identified by comparison of their retention times and their infrared and nmr spectra with those of authentic samples synthesized for this purpose. When the amount of acetate or alcohol was too small or its resolution on the gas chromatogram was too poor to make collection feasible, the material was tentatively identified by mixed gas chromatography with authentic samples.

Acetolysis of Bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl *p*-Bromobenzenesulfonate (2b).—The gas chromatogram of the acetolysis concentrate prior to distillation shows nine peaks, four of which, judging from their relatively long retention times, were due to diacetates. They were not characterized. The *first* component, although not present in sufficient amount to permit identification, is not an acetolysis product since it is also formed when a mixture of acetic acid, sodium acetate, acetic anhydride, and sodium *p*-bromobenzenesulfonate is heated for several hours at 115°. The *second* and *third* peaks were shown, by collection and comparison with authentic samples, to be due to *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl acetate (**5c**) and bicyclo[2.2.1]-

(45) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965).

(46) If the magnitude of $k_2[AcO^-]$ is comparable to that of $k_1 + k_3[AcOH]$, a first-order plot will deviate from linearity in the latter stages of the reaction. We estimate that our plots would have been perceptibly nonlinear at 70% reaction if $(k_1 + k_3[AcOH])/k_2 \leq 0.02$.

hept-2-ene-*syn*-7-methyl acetate (**2c**), respectively. The retention time of the *fourth* peak is identical with that of authentic bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**)[22] and, although the collected material was contaminated with a large amount of the immediately preceding acetate **2c**, the infrared spectrum shows strong absorptions at 1083, 1038, 1014 (sh), and 704 cm^{-1}, as well as some weaker ones which are characteristic of **7c**. From the infrared and nmr spectra of the collected material it appears that the *fifth* gas chromatographic peak is due primarily to a mixture of bicyclo[3.2.1]oct-3-en-*endo*- and -*exo*-2-yl acetates (**10c** and **11c**, respectively);[23] however, we believe that the collected material also contains small amounts of tricyclo[2.2.1.$0^{2,6}$]-heptane-3-methyl acetate (**9c**)[18] and an unknown acetate **8c** whose retention time is identical with that of bicyclo[2.2.2]oct-5-en-*endo*-2-yl acetate (**6c**)[23] (see below). The acetolysis concentrate was shown by mixed gas chromatography with authentic samples to contain no significant quantity (~0.1%) of tricyclo-[2.2.2.$0^{2,6}$]oct-*exo*- or -*endo*-3-yl acetates (**13c** and **12c**, respectively).[22]

The gas chromatogram of the reduced acetolysis concentrate exhibited six peaks which could be attributed to monoalcohols. The *first*, *fourth*, *fifth*, and *sixth* peaks were shown to be due to *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**5a**), bicyclo-[3.2.1]oct-3-en-*exo*- and -*endo*-2-ols (**11c** and **10c**),[23] and tricyclo-[2.2.1.$0^{2,6}$]heptane-3-methanol (**9a**),[18] respectively, by comparison of their retention times and their infrared and/or nmr spectra with those of known samples. Although the retention time of the *second* peak corresponds to that of authentic bicyclo[2.2.2]-oct-5-en-*endo*-2-ol (**6a**)[23] the infrared spectrum of the collected material, though weak, exhibits none of the absorptions at 3590 (O–H··π), 3048, ~1630 (w), 1404, 718 (–HC=CH–), 1082, 1058, and 1032 cm^{-1} (C–O) which are characteristic of **6a**. Instead, there are absorptions at 3620 (O–H, nonbonded), 3400 (broad, O–H, bonded), 1750 (w), and 1093 cm^{-1} (>CH–OH?). Thus we suspect that **8a** is a saturated and hence probably tricyclic secondary alcohol which contains no cyclopropane-type hydrogens (*i.e.*, no absorptions in the 3050–3000-cm^{-1} region). The retention time of the *third* alcohol peak is identical with that of authentic bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) and bicyclo[2.2.2]oct-5-en-*exo*-2-ol (**7a**).[22] Even though the collected material exhibits infrared and nmr spectra which are identical within experimental error (±5% estimated) with those of **2a**, we suspect that it also contains a small amount (~0.5%) of **7a** since the unreduced acetate mixture apparently contains a similar amount of **7c** (peak 4).

In order to provide an additional check on its composition, the *fifth* peak in the acetate chromatogram was collected, reduced separately with lithium aluminum hydride, and analyzed by isothermal gas chromatography on the 8-ft Carbowax column[41] at 135°. The resulting chromatogram exhibited four peaks in the relative proportion of 0.5, 6.5, 2.5, and 1.0 which correspond to **8a**, **11a**, **10a**, and **9a**, respectively.

An authentic sample of bicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (**3a**), when added to the reduced acetolysis mixture, is separated from all the other alcohols; thus the *anti* acetate **3c** cannot have been formed during the acetolysis of the *syn* brosylate **2b**.

Acetolysis of Bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl *p*-Bromobenzenesulfonate (3b).—The gas chromatogram of the concentrated but undistilled acetolysis mixture showed ten distinct peaks, the latter four of which were judged to be diacetates from their relatively long retention times. The *first* peak is identical with the first peak in the acetolysis mixture from the *syn* brosylate **2b** and hence is not a solvolysis product. The *second*, *third*, and *fifth* peaks were shown by comparison with authentic samples to be due to *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-yl acetate (**5c**), bicyclo[2.2.1]hept-2-ene-*anti*-7-methyl acetate (**3c**), and tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**), respectively. This latter acetate was present in an appreciable amount only in the 10-half-life sample (Table V). The retention time of the *fourth* peak was identical with that of authentic bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**).[22] The *sixth* peak was present in the 0.44-half-life acetolysis concentrate but was absent in the 10-half-life sample (Table V). Its retention time was identical with that of an authentic mixture of tricyclo[2.2.2.$0^{2,6}$]oct-*exo*- and -*endo*-3-yl acetates (**13c** and **12c**, respectively),[22] which are not themselves resolved under these conditions. An infrared spectrum of the collected material was identical with that of an authentic sample of essentially pure tricyclo[2.2.2.$0^{2,6}$]oct-*endo*-3-yl acetate (**12c**).[47]

The acetolysis concentrates were shown by mixed gas chromatography with authentic samples to contain no bicyclo[2.2.2]-oct-5-en-*endo*-2-yl acetate (**6c**)[23] or any of the bicyclo[3.2.1]oct-3-en-*endo*- or -*exo*-2-yl acetates (**10c** and **11c**, respectively).[23]

The gas chromatogram of the reduced acetolysis concentrate exhibits five peaks which could be attributed to monoalcohols. The *first*, *third*, and *fourth* peaks were shown by collection and comparison with authentic samples to be *syn*-7-methylbicyclo-[2.2.1]hept-2-en-*anti*-7-ol (**5a**), bicyclo[2.2.2]oct-5-en-*exo*-2-ol (**7a**), and bicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (**3a**), respectively. The *second* peak was not present in the reduced concentrates in a sufficient amount to permit isolation (Table V); however, its retention time is identical with that of authentic bicyclo[3.2.1]oct-6-en-*exo*-2-ol (**14a**).[22] The corresponding acetate, **14c**, was not detected in the acetolysis concentrate, but its retention time is such that it would have been masked by the *anti* acetate **3c**. The *sixth* peak in the reduced acetolysis concentrate was not collected but its retention time is identical with those of authentic tricyclo[2.2.2.$0^{2,6}$]octan-*endo*-3-ol (**12a**)[22] and tricyclo[2.2.1.$0^{2,6}$]heptane-3-methanol (**9a**).

Mixed gas chromatography of the reduced acetolysis concentrate with an authentic sample of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**2a**) confirmed that the *syn* acetate **2c** is not formed during the acetolysis of the *anti* brosylate **3b**.

Stability Studies of Acetolysis Products.—Samples (20 mg) of the following acetates were dissolved in 5 ml of anhydrous acetic acid (0.024 *M* in ester) containing 0.033 *M* sodium acetate and ~1% acetic anhydride. The solutions were heated at 115° for 8–10 days, the acetates were isolated in the usual manner, and the concentrated acetolysis mixtures were analyzed for monoacetates as before on the 20-ft Carbowax column.[41] Products were identified by comparison of their retention times and infrared spectra with those of known samples. Where necessary, the esters were reduced with lithium aluminum hydride, and the resulting alcohols were analyzed on the 8-ft Carbowax column.[41]

Under these conditions bicyclo[2.2.1]hept-2-ene-*syn*-7-methyl acetate (**2c**) gave a mixture of monoacetates consisting of about 0.5% of an acetate whose retention time and infrared spectrum were identical with those of tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**) and 99.5% of unchanged **2c**. Similarly, bicyclo-[2.2.1]hept-2-ene-*anti*-7-methyl acetate (**3c**) gave a mixture consisting of 3.5% **9c** and 96.5% **3c**. *syn*-7-Methylbicyclo[2.2.1]-hept-*anti*-7-yl acetate (**5c**) gave no new acetates when treated in this manner, and both bicyclo[2.2.2]oct-5-en-*exo*- and -*endo*-2-yl acetates (**7c** and **6c**, respectively) were recovered unchanged. Bicyclo[3.2.1]oct-3-en-*exo*-2-yl acetate (**11c**) was converted to a mixture of two monoacetates which upon reduction gave a 30:70 mixture of bicyclo[3.2.1]oct-3-en-*endo*- and -*exo*-2-ols (**10a** and **11a**, respectively). When tricyclo[2.2.2.$0^{2,6}$]oct-*endo*-3-yl acetate (**12c**) was treated similarly, it was completely converted into a mixture composed of 84% bicyclo[2.2.2]oct-5-en-*exo*-2-yl acetate (**7c**) and 16% bicyclo[3.2.1]oct-6-en-*exo*-2-yl acetate (**14c**).

Since tricyclo[2.2.1.$0^{2,6}$]heptane-3-methyl acetate (**9c**) is clearly not a primary acetolysis product, we did not test its stability, but it apparently would be stable under our solvolysis conditions.[18]

Acetolysis of Bicyclo[2.2.1]heptane-7-methyl *p*-Bromobenzenesulfonate (4b).—The gas chromatogram of the concentrated but undistilled acetolysis mixtures showed four peaks, the *first* of which is identical with the first component from the *syn* and *anti* brosylate-solvolysis mixtures, and hence is not a product of the acetolysis. The *second* and *third* peaks were collected and shown to be identical with 7-methylbicyclo[2.2.1]hept-7-yl acetate (**15c**) and bicyclo[2.2.1]heptane-7-methyl acetate (**4c**), respectively. Judging from the infrared and nmr spectra of the collected material, the *fourth* peak is composed of a mixture of secondary acetates. Its retention time is identical with those of authentic bicyclo[3.2.1]oct-*exo*-2-yl acetate (**17c**) and bicyclo-[2.2.2]oct-2-yl acetate (**18c**).

The gas chromatograms of the reduced acetolysis concentrates show four peaks which can be attributed to solvolysis products. They were identified by comparison of their retention times and spectra as 7-methylbicyclo[2.2.1]heptan-7-ol (**15a**), bicyclo-[3.2.1]octan-*exo*-2-ol (**17a**), bicyclo[2.2.2]octan-2-ol (**18a**), and bicyclo[2.2.1]heptane-7-methanol (**4a**). The infrared spectrum of collected **17a** is identical with that of authentic material and shows no evidence of the presence of bicyclo[3.2.1]octan-*endo*-2-ol

(47) We thank Dr. N. A LeBel of Wayne State University for a generous sample of this material.

(16a).[23a] These epimeric alcohols are not separated under our gas chromatographic conditions.

The Ionization Constants of the Bicyclic Acids.—The ionization constants of bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylic acid (**22**),[42] bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxylic acid (**23**),[42] and bicyclo[2.2.1]heptane-7-carboxylic acid (**24**)[42] were determined by potentiometric titration according to the procedure of Albert and Serjeant.[48] Standard aqueous solutions of the carboxylic acids (~0.01 *M* in acid) were titrated with 0.1 *N* standard sodium hydroxide using a glass *vs.* a standard calomel electrode in conjunction with a Beckman Model G pH Meter. The pK_a values are recorded in Table VII. They represent averages of 20–30 readings and two to four determinations each.

(48) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p 16 ff.

Acknowledgment.—It is a pleasure to acknowledge the financial support given this work by the Petroleum Research Fund of the American Chemical Society, Grant No. 911-A4.

The Reactions of Phosphorus Compounds. XII.[1] A New Synthesis of 1,2,3-Triazoles and Diazo Esters from Phosphorus Ylids and Azides

GEORGE R. HARVEY

Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166

Received December 3, 1965

Acylmethylenetriphenylphosphoranes react with organic azides to furnish either 1,5-disubstituted 1,2,3-triazoles or α-diazocarbonyl compounds in high yield. The course of the reaction depends upon the nature of the carbonyl group of the ylid. The mechanism and scope of the reaction are discussed. The 1-tosyltriazoles produced from tosyl azide solvolyze readily in hot ethanol to generate 5-substituted triazoles and ethyl tosylate.

The reaction of phosphorus ylids with organic azides would be expected to parallel the reactions of phosphines,[2] Grignard reagents,[3] and carbanions[4] with azides. In these three cases nucleophilic attack occurs on the azide terminus to give initially a triazo intermediate **1** which is either stable[3] or decomposes to other

$$Y^- + N_3R \longrightarrow \underset{\mathbf{1}}{Y\text{-}N{=}N\text{-}\bar{N}\text{-}R} \longrightarrow \text{products}$$

products.[2,4] Indeed, adducts from acyl ylids and organic azides fall within this latter group and their mode of decomposition depends upon the electrophilicity of the carbonyl group of the ylid. When the carbonyl moiety of the ylid is a ketone the triazo intermediate [**1**, Y = $(C_6H_5)_3P^+\text{CHC}(=O)R$] decomposes to a vicinal triazole. If the carbonyl group of this intermediate is an ester or amide, collapse to a diazo compound occurs. This paper discusses these two new reactions in terms of the common triazo intermediate.

Acylmethylenetriphenylphosphoranes **2** react with acyl and aryl azides **3** at ambient temperatures to furnish 1,5-disubstituted *v*-triazoles (**4**) in high yield. The products are tabulated in Chart I.

Qualitative observations of reactivity, as determined by the time required for complete reaction (see Table I), suggest nucleophilic attack of the ylid on the terminus of the azide.[2-4] The order of reactivity is dependent upon the electron-donating character of the R group in **2** (CH_3 > C_6H_5 > *p*-$NO_2C_6H_4$).[5] This is easily seen from the first three reaction times recorded in Table I. The *p*-nitrophenacyl ylid **2c** required 10 hr (infrared monitor) with tosyl azide to obtain the triazole **4c**; the acetonyl ylid **2a** required only 15 min for complete conversion to triazole **4a**. These observations are in accord with the reported basicities of the ylids.[5]

CHART I

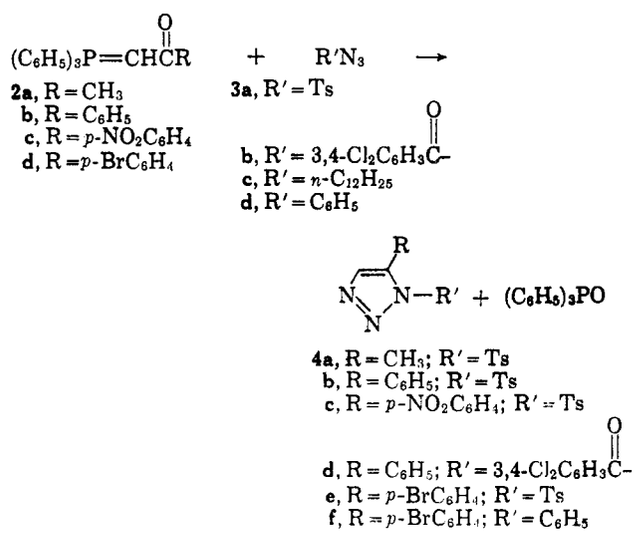
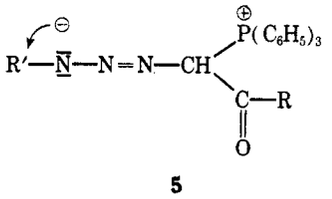


CHART II



5

The adduct from tosyl azide (**5**, R' = *p*-$CH_3C_6H_4SO_2$–; see Chart II) can delocalize the electron pair *via* p–d overlap with the sulfonyl group thus diminishing the reversibility of the reaction. Similar resonance stabilization is possible in the adduct from benzoyl azide. However, when R' is alkyl, *e.g.*, **3c**, or aryl, **3d**, no such

(1) Paper XI: A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **87**, 5603 (1965).

(2) (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); (b) J. E. Franz and C. Osuch, *Tetrahedron Letters*, **13**, 841 (1963).

(3) O. Dimroth, *Chem. Ber.*, **38**, 670 (1905).

(4) A. M. van Leusen, P. M. Smid, and J. Strating, *Tetrahedron Letters*, **6**, 337 (1965).

(5) For discussions of ylid basicities, see (a) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963); (b) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).