aluminum oxide to give 40 mg (80%) of **20c**. A solution of **22c** (70 mg) in PhH (10 mL) was added with 3 drops of TFA under cooling on an ice bath and the mixture was kept for 1 h at room temperature. The solvent was removed under reduced pressure at room temperature and the residue was found to contain 60 mg (86%) of **20c** (silica gel column chromatography). Compound **22c** (100 mg) was refluxed with xylene (5 mL) for 15 min. The deposited crystals were recrystallized from 50% EtOH to give 55 mg (55%) of **4c**.

A mixture of **22c** (200 mg) and $Na_2S_2O_4$ (202 mg) in 33% EtOH (40 mL) was stirred for 3 h at room temperature and acidified with 10% HCl. EtOH was removed in vacuo and saturated aqueous $NaHCO_3$ (1 mL) was added and the mixture was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The residue was chromatographed over aluminum oxide with Et_2O–hexane (1:2) to give 20 mg (16%) of 2,5-dimethyl-1-phenylaminopyrrole (mp 89–90 °C, needles from hexane)[24] [IR (KBr) 3280, 3040, 2920, 1620, 1500 cm^{-1}; NMR (CCl_4) δ 2.06 (6 H, s, CH_3 × 2), 5.63 (2 H, s, 3- and 4-H), 6.13 (1 H, br s, NH), 6.32 (2 H, m, Ar-H), 6.78 (1 H, m, Ar-H), 7.11 (2 H, m, Ar-H)], together with 10 mg (17%) of $PhNH_2$ and 20 mg (10%) of **20c**. The crystal data of a single crystal of **22c** are as follows: space group $P2_1/n$, a = 11.062, b = 15.310, c = 4.642 Å, β = 93.612°, and Z = 2. Analysis was carried on 1074 independent reflections with $I > 3\sigma(I)$, within the limit $\theta < 70°$, which were obtained by a Philips automatic diffractometer using Cu Kα radiation. The structure was solved by the direct method[13] and the final R factor was 0.05 (refined by block diagonal least-squares method; see paragraph on supplementary material at the end of this paper).

(24) J. R. Kenneth, U.S. Patent 2725378; *Chem. Abstr.*, **51**, 910 (1957).

Acknowledgment. We thank a referee for his helpful suggestion on the mechanism of the conversion of **22c**.

Registry No. 1a, 68321-99-3; **1b**, 68322-00-9; **1c**, 25233-87-8; **2a**, 66252-15-1; **2b**, 68322-02-1; **2c**, 68322-03-2; **3a**, 19194-90-2; **3b**, 68322-01-0; **3c**, 62260-20-2; **4a**, 71118-25-7; **4b**, 71118-26-8; **4c**, 71118-27-9; **4d**, 71118-28-0; **5a**, 55086-61-8; **5b**, 2048-69-3; **6a**, 26331-58-8; **6c**, 61208-80-8; **7a**, 30829-18-6; **8**, 71118-29-1; **9b**, 30842-90-1; **9c**, 1006-65-1; **9d**, 288-14-2; **10c**, 873-67-6; **11c**, 5585-14-8; **15a**, 4436-75-3; **20c**, 71118-30-4; **20d**, 71118-31-5; **21c**, 71118-32-6; **21d**, 71118-33-7; **22c**, 71118-34-8; **22d**, 71118-35-9; 2,5-dimethyl-1-phenylaminopyrrole, 32570-25-5; 1-methyl-4-phenyl-2-butene-1,4-dione, 26480-56-8; 1,4-diphenyl-2-butene-1,4-dione, 4070-75-1; 3,6-diphenylpyridazine, 891-22-5; 3,6-diphenylpyridazine 1-oxide, 21111-33-1.

Supplementary Material Available: Tables of positional and thermal parameters, and interatomic distances and bond angles for the structure of the compound **22c** (2 pages). Ordering information is given on any current masthead page.

Acetolysis of the Isomeric 5,6-Dimethylnorbornyl *p*-Bromobenzenesulfonates[1a]

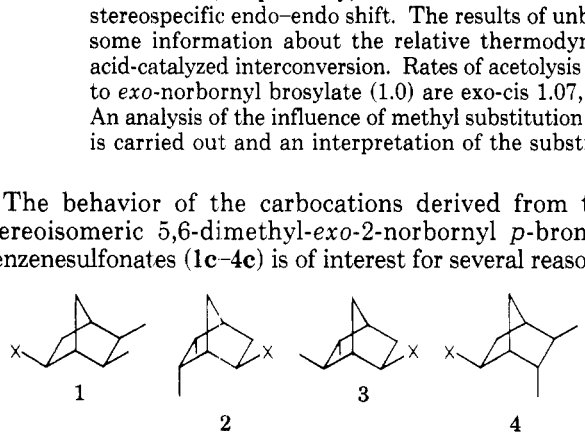
Allan K. Colter*[1b] and Robert A. Reith

Departments of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and the University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received March 26, 1979

The products of acetolysis of the four stereoisomeric 5,6-dimethyl-*exo*-2-norbornyl brosylates and of acid-catalyzed addition of acetic acid to the three stereoisomeric 5,6-dimethylnorbornenes have been investigated. Acetolysis of the two Wagner–Meerwein (WM)-related *cis*-brosylates under kinetically controlled conditions led to identical product mixtures from which four acetates and one olefin, accounting for >99% of the products, were identified. Under similar conditions two different mixtures of known composition of the WM-related *trans*-brosylates also gave identical product mixtures, from which two acetates and one olefin, accounting for >99% of the products, were identified. The proportions of the total product arising from 6,2 hydride shift under these conditions are 93 and 57%, respectively, in the cis and trans series, these products arising almost exclusively from a single stereospecific endo–endo shift. The results of unbuffered acetolyses and acid-catalyzed olefin additions provide some information about the relative thermodynamic stabilities of the products and their relative rates of acid-catalyzed interconversion. Rates of acetolysis of the 5,6-dimethyl-*exo*-2-norbornyl brosylates at 25 °C relative to *exo*-norbornyl brosylate (1.0) are exo-cis 1.07, endo-cis 0.37, endo-5,exo-6 0.76, and exo-5,endo-6 <ca. 0.04. An analysis of the influence of methyl substitution at each of the four C5 and C6 positions on the rate of acetolysis is carried out and an interpretation of the substituent effects offered.

The behavior of the carbocations derived from the stereoisomeric 5,6-dimethyl-*exo*-2-norbornyl *p*-bromobenzenesulfonates (**1c**–**4c**) is of interest for several reasons.



1 2 3 4

a, X = OH; b, X = OAc; c, X = OBs

These systems provide one of the simplest tests of the stereospecificity of transannular (6,2) hydride shifts in norbornyl cations. A strong preference for endo–endo hydride migration has been demonstrated in solvolysis of more complex substrates[2,3] and in methyl- and dimethylnorbornyl cations in superacid media.[4] The products of the solvolyses of **1c**–**4c** are also of interest in relation to the influence of substitution on the relative rates of reaction of nucleophiles at WM-related sites[3d,5] and

(1) (a) Abstracted in part from the Ph.D. Thesis of Robert A. Reith, Carnegie-Mellon University. (b) Address correspondence to this author at the Department of Chemistry, University of Guelph.

(2) J. A. Berson and P. W. Grubb, *J. Am. Chem. Soc.*, **87**, 4016 (1965).

(3) (a) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **88**, 1556 (1966); (b) B. M. Benjamin, B. W. Ponder, and C. J. Collins, *ibid.*, **88**, 1558 (1966); (c) B. M. Benjamin and C. J. Collins, *Tetrahedron Lett.*, 5477 (1966); (d) C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **89**, 1652 (1967).

(4) (a) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **94**, 1780 (1972); (b) R. Haseltine, N. Wong, T. S. Sorensen, and A. J. Jones, *Can. J. Chem.*, **53**, 1891 (1975).

(5) (a) A. K. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965); (b) J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **89**, 2573 (1967); (c) P. G. Gassman and J. M. Hornback, *ibid.*, **94**, 7010 (1972); (d) D. C. Kleinfelter, M. B. Watsky, and W. E. Wilde, *J. Org. Chem.*, **38**, 4134 (1973).

0022-3263/79/1944-3529$01.00/0

Table I. Products of Brosylate Acetolyses and Acetic Acid Additions in the Cis Series

sub-str[a]	con-di-tions	products, mol %							
			single 6,2-shift			multiple 6,2-shifts		unidentified	
		WM rearr 1b	11	15	8	12	9	acetate	hydro-carbon
1c	*b*	5.6 ± 0.6	28.0 ± 3.5	58.5 ± 2.0	6.6 ± 1.2	0.8 ± 0.1		0.6 ± 0.5	
2c	*c*	5.6 ± 0.3	28.4 ± 1.3	58.4 ± 1.3	6.7 ± 0.7	0.8 ± 0.1			
2c	*d*	5.4	9.9	71.8	9.3	3.0	trace	0.7	
2c	*e*	3.6	8.9	73.4	9.8	3.3	0.5	0.4	
2c	*f*	5.9			53.3		39.0		1.7
2c	*g*	5.7			44.2		48.0		2.1
5	*h*	18.0	1.8		50.9	13.7	15.0	0.7	
6	*i*	16.4	4.3		48.0	13.1	16.6	1.6	
6	*j*	19.7	trace		49.3	7.5	23.5		
6	*k*	13.6	trace		54.3	trace	31.8	0.4	

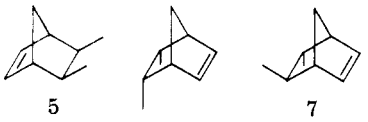
[a] [Brosylate] = 0.1 M, [olefin] = 0.16 M. [b] 40 °C, 5 or 15 h, 0.2 M sodium acetate, average of 2 runs. [c] Same as footnote *b*, average of 3 runs. [d] 40 °C, 10 h, 0.2 M urea. [e] 40 °C, 20 h, 0.2 M urea. [f] 40 °C, 10 h, unbuffered. [g] 40 °C, 20 h, unbuffered. [h–k] Acetic acid, 1.5×10^{-2} M H_2SO_4, 60 °C: [h] 45.1%, [i] 16.2%, [j] 37.5%, [k] 65.4% conversion of olefin to acetate.

on the competition between solvent capture and 6,2 (or 6,1) hydride shift.[3d,5,6] Finally, the rates of solvolysis of **1c–4c** could shed some light on the still incompletely understood influence of methyl substitution at C5 and C6 on solvolytic reactivity.[5a,7]

We report here a study of the products of acetolysis of **1c**, **2c**, and two different mixtures of known compositions of **3c** and **4c**, under conditions of kinetic control of products and under conditions of partial equilibration, and of the products of acid-catalyzed addition to the three isomeric 5,6-dimethylnorbornenes, under conditions of parital equilibration. We report also the results of a less detailed study of the kinetics of acetolysis of **1c**, **2c**, and the two mixtures of **3c** and **4c**.

Results

The alcohols **1a–4a** were prepared by hydroboration–oxidation of the known[8] 5,6-dimethylnorbornenes **5–7**.



5 6 7

Purification of the hydroboration products from **5** and **6** through their acid phthalates led to pure (GC, NMR) samples of **1a** and **2a**. Hydroboration of **7** led to a 46:54 mixture of **3a** and **4a**. Partial separation was achieved by fractional crystallization of this mixture, leading to an 88:12 mixture of **3a** and **4a**. The 46:54 and 88:12 mixtures of **3a** and **4a** were used in all subsequent experiments.

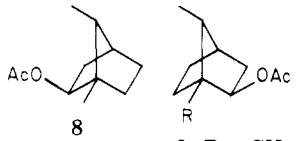
The products of the acetolyses of **1c**, **2c**, and the 46:54 and 88:12 mixtures of **3c** and **4c** were examined in acetic acid–0.20 M sodium acetate at 40 °C. The product compositions from **1c** and **2c** were unchanged by a threefold variation in reaction time, confirming the stabilities of the products under these conditions. In order to obtain some information about the products under less basic conditions and about the changes in composition resulting from partial equilibration, the products of the acetolysis of **2c** were examined also in acetic acid–0.20 M urea[9] at 40 °C, and the products of the acetolyses of **2c** and the 46:54 mixtures of **3c** and **4c** were examined in unbuffered acetic acid at 40 °C. Finally, the products of the acid-catalyzed addition of acetic acid to **5**, **6**, and **7** at 60 °C were examined.

The results of the product studies in the cis series (**1c**, **2c**, **5**, **6**) are summarized in Table I; those involving the trans series (**3c**, **4c**, **7**) are summarized in Table II. The products are grouped according to their proposed origin (Discussion, Scheme II).

All of the products were isolated by preparative GC, and structural assignments are based on NMR, IR, and mass spectra. Since the NMR spectra are of key importance in the structural assignments, they are considered in more detail below.

The 60-MHz proton NMR spectra of acetates **1b–4b** are very similar (Experimental Section) except for the low-field multiplets due to the C2 hydrogens. These absorptions appear at 4.58 and 4.90 ppm in **1b** and **2b**, respectively. This difference, attributed to a deshielding effect of an *endo*-6-methyl, was used to distinguish **3b** and **4b**, in which the C2 proton multiplets are centered at 4.48 and 4.90 ppm, respectively. Similar differences appear in the spectra of the corresponding alcohols and brosylates and in the spectra of *endo*-6-methyl-*exo*-2-norbornanol[10] and *exo*-2-norbornanol.[11]

The NMR spectra of the compounds identified as β-santenyl acetate (**8**) and α-santenyl acetate (**9**) are identical, except for small chemical shift differences, with the spectra of these compounds reported by Hatfield and Huntsman.[12,13] Additional evidence for these structural



8

9, R = CH_3
10, R = H

(6) (a) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); (b) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831 (1966); (c) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967); (d) H. L. Goering and M. J. Degani, *ibid.*, **91**, 4506 (1969).

(7) (a) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.* **87**, 375 (1965); (b) J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **88**, 1067 (1966); (c) C. F. Wilcox, Jr., L. M. Loew, R. G. Jesaitis, S. Belin, and J. N. C. Hsu, *ibid.*, **96**, 4061 (1974); (d) G. D. Sargent, *Carbonium Ions*, **3**, 1099 (1973); (e) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977.

(8) (a) K. Alder, W. Roth, and A. Grell, *Chem. Ber.*, **88**, 407 (1955); (b) H. N. Miller and K. W. Greenlee, *J. Org. Chem.*, **26**, 3734 (1961).

(9) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967).

(10) D. E. Gwynn and L. Skillern, *Chem. Commun.*, 490 (1968).

(11) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

(12) L. D. Hatfield and W. D. Huntsman, *J. Org. Chem.*, **32**, 844 (1967).

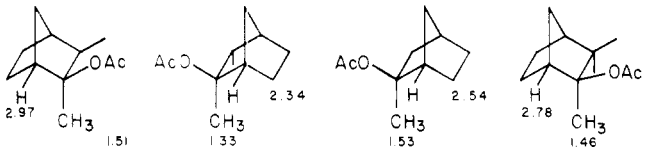
Table II. Products of Brosylate Acetolyses and Acetic Acid Additions in the Trans Series

substr[a]	conditions	products, mol % WM rearr 3b	WM rearr 4b	single 6,2-shift 16	single 6,2-shift 9	multiple 6,2-shifts 11	multiple 6,2-shifts 8	unidentified acetate	unidentified hydrocarbon
3c:4c, 46:54	*b*	37.9 ± 0.7	3.0 ± 0.3	58.8 ± 0.5				0.4 ± 0.1	
3c:4c, 88:12	*c*	42.5	2.6	53.7				1.2	
3c:4c, 46:54	*d*	13.7	*g*		73.0		10.1		3.2
7	*e*	38.3	*g*		55.4	2.9	3.4		
7	*f*	34.6	*g*		58.7	1.4	5.3		

[a] [Brosylate] = 0.1 M, [olefin] = 0.16 M. [b] 40 °C, 5 h, 0.2 M sodium acetate, average of 2 runs. [c] 40 °C, 5 h, 0.2 M sodium acetate. [d] 40 °C, 20 h, unbuffered. [e,f] Acetic acid, 1.5 × 10^{-2} M H_2SO_4, 60 °C; [e] 18.9%, [f] 34.6% conversion of **7** to acetate. [g] Small amount could be obscured under peak for **9** (see text).

assignments is the striking similarity of the spectrum of **9** with that of **10**,[14] except for the absorption due to the C1 methyl. Particularly significant in these spectra is the appearance of the C2 proton multiplet around 4.6–4.7 ppm. In the spectra of **9** and **10** this absorption is a clean doublet of doublets ($J_{2,exo-3} \approx 3$ Hz, $J_{2,endo-3} \approx 7$ Hz); the absorption due to the C2 proton of **8** appears as a more complex multiplet due to coupling with the anti-C7 proton.[15]

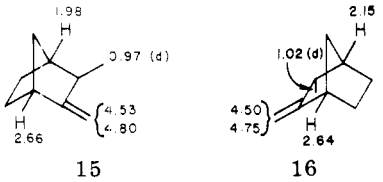
The final two acetate products, assigned structures **11** and **12**, are tertiary acetates, as indicated by the absence of any absorption in the 4.5–5.0-ppm region characteristic of secondary *exo*-norbornyl acetates. The principal distinguishing features are the chemical shifts of the C1 protons and the C2 methyl protons. These are compared with data for the related compounds 2-methyl-*exo*-2-norbornyl acetate (**13**)[14,16] and camphene hydrate acetate (**14**).[16] The lower field absorption of the C1 proton in **11**



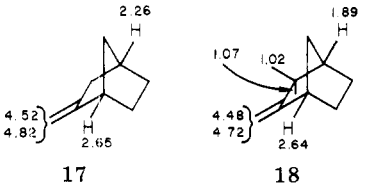
11 12 13 14

and **14** compared to that of **12** and **13** is attributed to an enhanced deshielding effect of the acetate group resulting from restriction of its rotational freedom by the *exo*-3-methyl. Also consistent with these structural assignments is the small shielding effect of an *endo*-3-methyl on the *endo*-2-methyl.

The two principal olefinic products were identified as *exo*-isosantene (**15**) and *endo*-isosantene (**16**) from IR and

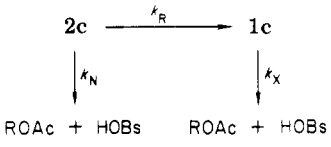


15 16



17 18

Scheme I



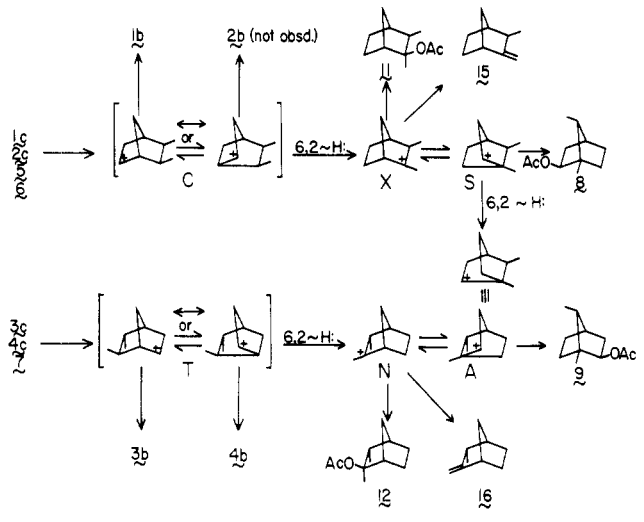
NMR spectral data. The chemical shifts (ppm) of the assignable absorptions are compared with those of 2-methylenenorbornene (**17**)[17] and camphene (**18**).[18] The principal differences in the spectra of **15** and **16** are the chemical shifts of the C4 protons and the C3 methyl protons. The difference in the C4 proton chemical shifts (**15** and **18** vs. **16** and **17**) is ascribed to a shielding effect of an *exo*-3-methyl. There are numerous examples of this effect in both norbornenes and norbornanes. For example, the bridgehead protons in **5** and **6** absorb at 2.35 and 2.64 ppm, respectively, while those in **7** absorb at 2.22 and 2.60 ppm. The isosantenes **15** and **16** are known; however, we could find only one report[19] of proton NMR and infrared data for these compounds. Our spectral data for **15** and **16** are in close agreement with those reported by Degny et al. for **16** and **15**, respectively, and we conclude that their spectral data for these two compounds should be interchanged.

The kinetics of the acetolyses of **1c**, **2c**, and the 46:54 and 88:12 mixtures of **3c** and **4c** were investigated at 25 °C. The acetolysis of **1c** followed first-order kinetics through 3 half-lives, free from any complications due to ion-pair return. In contrast, first-order rate constants for the acetolysis of **2c**, calculated in the usual way, showed a regular increase with increasing percent reaction from ca. 4 × 10^{-5} s^{-1} over the first 20% to ca. 7 × 10^{-5} s^{-1} after 75% reaction. These results suggest that solvolysis is accompanied by ion-pair return to a more reactive brosylate, presumably **1c**. Although ion-pair return following a 6,2 hydride shift is also a possible complication,[6d,20] the fact that the acetolysis of **1c** shows strict first-order behavior indicates that such return does not affect the kinetics.

The simplest representation of the acetolysis of **2c** which includes concurrent rearrangement to **1c** is Scheme I, in which k_X is the measured rate constant for the acetolysis of **1c**. All acetolysis products and **1c** presumably arise from a common intermediate or intermediates (ion **C**, Scheme II). The inclusion of additional intermediates affects the

(13) The absorptions due to the C2 and acetoxy protons are 0.10–0.13 ppm upfield in our spectra, measured in CCl_4, compared to those in ref 12, measured in $CDCl_3$.
(14) J. A. Berson, personal communication.
(15) (a) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963); (b) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).
(16) H.-J. Schneider, N. C. Franklin, and W. Hučkel, *Justus Liebigs Ann. Chem.*, **745**, 1 (1971).
(17) H. Krieger, *Suom. Kemistil. A*, **37**, 148 (1964).
(18) "Sadtler Standard NMR Spectra", Sadtler Research Laboratories, Philadelphia, PA, 1971, Spectrum 10614M.
(19) E. Degny, F. Petit, M. Evrard, and M. Blanchard, *Bull. Soc. Chim. Fr.*, 4770 (1972).
(20) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

Scheme II



interpretation of k_N, k_R, and k_X but not the analysis of the kinetic data. The data were analyzed by deriving an expression for the extent of solvolysis in terms of k_X, k_N, k_R, and t. With the measured value of k_X, best fit values of k_N and k_R were determined individually for three separate kinetic runs. Values of k_N and k_R so obtained were in reasonable agreement (average deviations 3.9 and 10.6%, respectively), and the experimental titers could be reproduced to average deviations of ±0.56, ±0.76, and ±0.93% by the best fit rate constants (Experimental Section).

It was hoped that the kinetic behavior of the two mixtures of **3c** and **4c** could provide estimates of the rates of acetolysis of the two esters. In theory, such estimates could be obtained from the initial rates for two mixtures of known composition, or even from the kinetic behavior of a single mixture of known composition. In this case, however, the initial rates of the two mixtures indicated that **3c** is at least 20-fold more reactive than **4c**. As a consequence, **4c** makes no contribution, within experimental error, to the initial rates of the two mixtures. Further, the kinetics of the acetolysis of **4c** are expected to be complicated by ion-pair return to **3c**, as in the acetolysis of **2c**. In agreement with expectation, the kinetic behavior of the two mixtures is more complex than that expected for a mixture of two compounds obeying simple first-order kinetics. In spite of these complications, a reasonable (±5%) estimate of the rate constant for **3c** could be obtained from the initial rate of acetolysis of the 88:12 mixture. For **4c**, only an approximate maximum rate constant could be estimated. The kinetic results are summarized in Table III.

Table III. Rates of Acetolysis of 5,6-Dimethyl-2-*exo*-norbornyl Brosylates at 25 °C

ester	$10^5 k_1$, s^{-1} [a]	rel rate [b]
1c	9.84 ± 0.03	1.07
2c	k_N 3.42 ± 0.14 [c] k_R 4.8 ± 0.5 [c]	0.37
3c	7.0 ± 0.2	0.76
4c	≤ca. 0.4	≤ca. 0.04

[a] Averages of 2 or 3 runs, with average deviations. [b] Rate relative to that of 2-*exo*-norbornyl brosylate, measured in this work as 9.17 ± 0.15 × 10^{-5} s^{-1}. [c] Rate constants defined in Scheme I.

Discussion

Much of the results summarized in Tables I and II confirm conclusions reached from earlier investigations of norbornyl cations. We summarize these conclusions below but restrict detailed discussion to those results which have no close analogy in earlier work.

All of the characterized products can be accounted for in a qualitative way in terms of Scheme II, which includes only Wagner–Meerwein (WM) rearrangement and stereospecific endo–endo 6,2 hydride shifts. The scheme is noncommittal on the question of the structure of secondary norbornyl cations in solvolytic media[7d,e] and is simplified by the omission of counterions. The identity of the products of the acetolyses of **1c** and **2c** and of the two mixtures of **3c** and **4c** under acetate-buffered conditions confirms earlier conclusions[3d,5a,d,21] that WM rearrangement is much faster than a 6,2 hydride shift. The products under acetate-buffered conditions also confirm the high endo–endo stereospecificity of 6,2 hydride shifts[2,3] in these systems.

The fraction of the first-formed cations (C and T) which undergo the 6,2 hydride shift before reaction with solvent in acetate-buffered acetolysis is 0.94 (C) and 0.54–0.59 (T). This difference is most plausibly attributed to differences in the rate constants for the 6,2 hydride shift. Repulsive nonbonded interactions between the two methyl groups in C are relieved, in part, in the transition state leading to X. No corresponding nonbonded interactions are present in T, and the product of the 6,2-shift, N, because of the preference of a methyl group for an exo orientation,[22] should be slightly higher in energy than X.

In the reaction of C and T with solvent there is a strong preference for formation of the product (**1b** and **3b**, respectively) having an *exo*-6-methyl. In the acetate-buffered acetolyses we estimate that the ratio of **1b** to **2b** is at least 50:1, while the ratio of **3b** to **4b** is (14 ± 2):1. This result, which parallels that obtained in the acetolysis of *endo*-6-methyl-*exo*-2-norbornyl brosylate,[5a] is relevant to the influence of 6-methyl substitution on the rates (discussed below).

The proportions of the three products 8, 11, and 15, considered to arise from the intermediates X and S, in the acetate-buffered acetolyses of **1c** and **2c** are unexceptional.[5b,23] Of the three corresponding products in the trans series, **9**, **12**, and **16**, only **16** was obtained in the acetate-buffered acetolyses of the **3c**, **4c** mixtures. The reason for the difference in the behavior of the ions N ⇌ A vs. X ⇌ S is not clear. In contrast to the behavior of the N ⇌ A pair generated from T via a single 6,2-shift, the same cation presumed to arise from C by two successive 6,2-shifts leads entirely to the tertiary acetate **12**. The intermediates generated by these two routes are clearly different in some way, probably in the position or proximity of the counterion, with the proportion of substitution increasing with increasing ion separation.[24]

The acetolysis of **2c** buffered by 0.2 M urea leads to a mixture of the same products as obtained in the acetate-buffered acetolysis, plus a small amount of α-santenyl acetate (**9**). The relative proportions of **8**, **11**, and **15** under these conditions are quite different, however, the main difference being a substantial increase in the proportion of olefin **15** at the expense of tertiary acetate **11**. The

(21) M. Saunders, P. von R. Schleyer and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).
(22) R. J. Ouellette, J. D. Rawn, and S. M. Jreissaty, *J. Am. Chem. Soc.*, **93**, 7117 (1971).
(23) (a) J. A. Berson, *Mol. Rearrangements*, 1, 133 ff (1963); (b) W. Hückel, H.-J. Schneider, and H. Schneider-Bernlöhr, *Justus Liebigs Ann. Chem.*, 1690 (1975); (c) C. A. Bunton and C. O'Connor, *Chem. Ind. (London)*, 1182 (1965); (d) H. C. Brown and S. Ikegami, *J. Am. Chem. Soc.*, **90**, 7122 (1968).
(24) M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963).

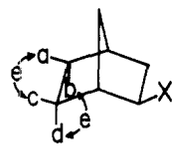


Figure 1. Influence of methyl substitution on rates of acetolysis.

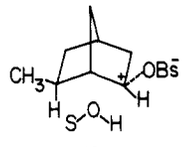
identity of the products obtained after 10 and 20 h shows that these differences are not a result of product instability.

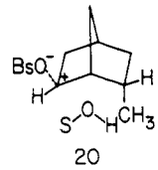
The products of the unbuffered acetolyses of **2c** show that under acidic conditions conversion of **11** and **15** to **8** occurs most rapidly, that conversion of **8** to **9** occurs more slowly, and that both occur under conditions where **1b** is stable. Unbuffered acetolysis of a **3c**–**4c** mixture led, after 20 h, to a mixture of **8** and **9**, with some decrease in **3b** and **4b**. Reaction of *cis*-2,3-dimethyl-*endo*-2-norbornanol with H_2SO_4 in acetic acid at 100 °C has been reported to yield a 19:79 mixture of **8** and **9**.[12]

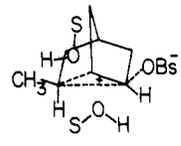
The product mixtures from the acetic acid additions are similar to those from the unbuffered acetolyses except that under the conditions of the addition reactions there is incomplete conversion of the tertiary acetates **11** and **12** to the related santenyl acetates **8** and **9**. The absence of any detectable **2b** in the additions to **5** and **6** and of any **4b** in the additions to **7** indicates that the products arise entirely from a carbocation intermediate (i.e., C or T) which is either bridged or which undergoes WM rearrangement more rapidly than reaction with solvent. However, the significantly smaller percent of 6,2-shift in the additions to **5** and **6** than in the acetolyses of **1c** and **2c** indicates that the intermediate is more capturable. For comparison with these results, Beckmann and Bamberger,[25a] on more vigorous treatment of **7** with an acetic acid–sulfuric acid mixture, obtained a mixture of acetates composed mainly (on the basis of isolation as the acid phthalates) of **9** and a *trans*-5,6-dimethyl-2-norbornyl acetate. Similar treatment of **15** and **16** led to **9** together with smaller amounts of **8**.[25b]

The data in Table III reveal substantial effects of 5- and 6-methyl substitution on the rates of acetolysis of *exo*-2-norbornyl brosylates. In our analysis of these effects we examine the rates of acetolysis of 5- and 6-methyl-substituted *exo*-2-norbornyl arenesulfonates at 25 °C relative to that of the corresponding *exo*-2-norbornyl arenesulfonate. In addition to the data in Table III, we have available the relative rates of 6,6-dimethyl-*exo*-2-norbornyl tosylate (4.0×10^{-2}),[7a] 5,5-dimethyl-*exo*-2-norbornyl brosylate (3.0×10^{-1}),[5a] and *exo*-6-methyl-*exo*-2-norbornyl tosylate (~0.5).[26] Let us assume, as a first trial, that the influences of substitution at the 5-exo, 5-endo, 6-exo, and 6-endo positions are completely independent and additive. Using the symbols *a*, *b*, *c*, and *d*, respectively (Figure 1), for the factors by which the rate is changed by substitution at the four positions, we can write an equation for each available relative rate, viz., ac = 1.07 (for **1c**), bd = 0.37 (for **2c**), and so on. It is immediately apparent that the data are not fitted by this simple model. For example, using the data for the 6-*exo*-methyl, 5,5-dimethyl, and 6,6-dimethyl esters and **3c** to obtain values of *a*, *b*, *c*, and *d*, the predicted relative rates of **1c** and **2c** (ac and bd, respectively) are much smaller than the experimental values. It is apparent, then, that a fifth parameter, *e*, for vicinal cis methyl groups is required. This model then leads to the following seven equations: ab = 0.30 (5,5-dimethyl), $cd = 4.0 \times 10^{-2}$ (6,6-dimethyl), ace = 1.07 (**1c**), bde = 0.37 (**2c**), bc = 0.76 (**3c**), $ad < 4 \times 10^{-2}$ (**4c**), and c = 0.5 (exo-6). Using the first five equations, which are based on the most precise data, we obtain a = 0.27, b = 1.1, c = 0.69, $d = 5.8 \times 10^{-2}$, and e = 5.7. These values in turn predict relative rates of 0.69 for the *exo*-6-methyl system and 1.6×10^{-2} for **4c**, in reasonable agreement with experiment. The qualitative conclusions are, therefore, that *endo*-6-methyl substitution leads to a strong rate depression, *exo*-5- and *exo*-6-methyl substitutions lead to a smaller rate depression, and *endo*-5-methyl substitution leads to a small rate enhancement. Finally, a substantial rate enhancement results from a vicinal cis arrangement of methyl groups.

The rate-retarding effect of 6,6-dimethyl substitution has been ascribed to an increase in the nonbonded repulsion between the methyl groups and the C1 and C2 hydrogens in movement toward a bridged ion.[7a] While such interactions may be important, they cannot account for the fact that the rate-retarding effect of an *endo*-6-methyl is about 12 times that of an *exo*-6-methyl. Adding approximately 0.9 kcal mol^{-1} for the contribution of an *endo*-methyl (compared to an *exo*-methyl) to the ground-state free energy,[22] we expect the transition states for ionization of the 6-*endo*- and 6-*exo*-arenesulfonates to differ by about 2.4 kcal mol^{-1}. This difference would require a *highly unsymmetrical* transition state for ionization since the exo–endo distinction is lost in a symmetrical bridged ion. If solvent capture is approximately the microscopic reverse of ionization, the difference in the effects of 6-*exo*- and 6-*endo*-methyl substitution on the rate is related to the predominant formation of 6-*exo*-methyl acetates from C and T and requires a similar explanation. One possible origin of the difference is steric hindrance to solvation (**19** vs. **20**). This model requires that most of


19


20


21

the positive charge in the transition state be localized at the position of leaving group departure, since if the charge is approximately equally distributed as in **21**, solvation from the two sides will be equally important. An alternative explanation, also requiring concentration of the positive charge at one carbon, is a combination of retardation due to nonbonded interactions (above) and an electron-supplying effect which is greater for an *exo*-methyl.[27]

While there is undoubltedly some contribution from electronic effects, the influence of methyl substitution at C5 and of vicinal *cis*-methyl substitution can be understood qualitatively in terms of a change in molecular geometry, with consequent changes in nonbonded interactions, accompanying ionization. In the formation of a bridged ion the exo–endo distinction between C5 methyl groups is lost. Consequently, bridging should be accompanied by a small increase in nonbonded repulsions (primarily with the *syn*-C7 hydrogen) for an *exo*-5-methyl and a small decrease in nonbonded repulsions (primarily with the *endo*-C3 hydrogen) for an *endo*-5-methyl. If this expectation is correct, larger endo-5 substituents should produce a larger steric enhancement of ionization. The unfavorable in-

(25) (a) S. Beckmann and R. Bamberger, *Justus Liebigs Ann. Chem.*, **574**, 76 (1951); (b) S. Beckmann and A. Dürkop, *ibid.*, **594**, 205 (1955).

(26) Private communication from P. von R. Schleyer to H. C. Brown, cited in ref 7e, p 196.

(27) (a) G. A. Olah, A. M. White, J. R. De Member, A. Commeyras, and C. Y. Lui, *J. Am. Chem. Soc.*, **92**, 4627 (1970); (b) G. A. Olah, J. R. De Member, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1442 (1971).

teraction between vicinal *cis*-methyl groups should also decrease on bridging. As noted above, a further decrease in nonbonded interactions must accompany a 6,2 hydride shift. The resulting increase in the rate constant for the 6,2-shift will result in a smaller increase in the observed rate constants for **1c** and **2c** by decreasing the fraction of C which returns to **1c**.

Experimental Section

All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and M-H-W Laboratories, Garden City, MI. Infrared spectra were measured with a Perkin-Elmer Model 137B spectrophotometer. NMR spectra were measured with a Varian A-60 spectrometer in CCl_4 solvent, unless otherwise specified, with tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS-9 high-resolution mass spectrometer at ionizing potentials of 14 and 70 eV.

***cis*-*exo*-5,6-Dimethylnorbornene (5), *cis*-*endo*-5,6-dimethylnorbornene (6), and *trans*-5,6-dimethylnorbornene (7)** were synthesized as described by Alder et al.[8a] with two minor modifications. The Diels–Alder adduct of maleic anhydride and cyclopentadiene, 5-norbornene-*endo*-2,3-dicarboxylic anhydride,[28] its isomerization product, 5-norbornene-*exo*-2,3-dicarboxylic anhydride,[29] and the Diels–Alder adduct of fumaryl chloride and cyclopentadiene, 5-norbornene-*trans*-2,3-dicarboxylic acid chloride,[30] were reduced directly to the corresponding 5,6-bis-(hydroxymethyl)norbornenes with lithium aluminum hydride in anhydrous ether rather than first being converted to the dimethyl 5-norbornene-2,3-dicarboxylates.[31] The 5,6-bis(hydroxymethyl)norbornenes were converted to the corresponding ditosylates by using the method of Marvell et al.[32]

Synthesis of the 5,6-Dimethyl-*exo*-2-norbornanols 1a, 2a, 3a, and 4a. To a solution of 20 g (0.16 mol) of **5**, **6**, or **7** in 180 mL of anhydrous THF was added 200 mL of a freshly prepared 1.67 M solution of diborane in THF over a period of 1 h with stirring and external cooling (−10 to −5 °C). The solution was stirred for 1 h at 0 °C and for 5 h at room temperature and cooled again to −5 to −10 °C, and 150 mL of 1 M aqueous NaOH, followed by 50 mL of 30% H_2O_2, was added in a dropwise manner. After the mixture was stirred for 2 days at room temperature, solid NaCl was added and the aqueous and organic phases were separated. The aqueous phase was extracted with six 50-mL portions of pentane. The THF and pentane solutions were combined, washed twice with saturated NaCl, with aqueous $FeSO_4$ until free of peroxides, and with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and filtered, and the solvent was removed with a rotary evaporator. The alcohols, obtained in nearly quantitative yield (approximately 23 g), were usually semisolids or viscous oils and were purified by conversion to their acid phthalates and subsequent saponification. Equimolar amounts of the alcohol and phthalic anhydride in anhydrous pyridine were heated on the steam bath for 5 h. After workup, the crude acid phthalates of **1a** and **2a** were crystallized once or twice from methanol–water and saponified with steam distillation of the alcohol from a 30% aqueous KOH solution.

Alcohol **1a**: mp 35–36 °C; NMR δ 0.80 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.84 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.0–1.9 (overlapping multiplets, 8 H), 3.03 (s, 1 H, OH), 3.70 (m, 1 H, C2 H); IR (CCl_4) 3570 cm^{-1} (OH). The acid phthalate of **1a** had mp 136.5–138 °C. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found: C, 70.5; H, 7.1.

Alcohol **2a**: mp 55–56 °C; NMR δ 0.77 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.83 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.0–2.2 (overlapping multiplets, 8 H), 3.38 (s, 1 H, OH), 3.95 (m, 1 H, C2 H); IR (CCl_4) 3570 cm^{-1} (OH). The acid phthalate of **2b** had mp 146.5–148 °C. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found: C, 70.6; H, 7.0.

Hydroboration of **7** led to a mixture of **3a** and **4a** in approximately equal amounts which could not be separated by GC using any of several columns. Acetylation of the crude alcohol mixture afforded an acetate mixture containing, by GC analysis, 46.4% **3b** and 53.6% **4b**. For removal of any impurities the crude alcohol mixture was converted to a mixture of acid phthalates, mp 125–170 °C, and then saponified without crystallization. The alcohol mixture so obtained (viscous oil) was unchanged in composition, as shown by acetylation and GC analysis of the acetate mixture. Four crystallizations of the first acid phthalate mixture led to material which had a constant melting point of 165–166.5 °C. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found: C, 70.5; H, 7.0. Saponification followed by acetylation gave a mixture of acetates containing, by GC analysis, 87.9% **3b** and 12.1% **4b**. The pure (GC) 46:54 and 88:12 mixtures of **3a** and **4a** were used in all subsequent product and kinetic studies.

Synthesis of 5,6-Dimethyl-*exo*-2-norbornyl Brosylates (1c, 2c, 3c, and 4c). The following procedure is typical. To a solution of 8.0 g (0.057 mol) of alcohol in 10 mL of anhydrous pyridine was slowly added 14.6 g (0.057 mol) of *p*-bromobenzenesulfonyl chloride. Shortly after complete solution of the sulfonyl chloride, the solution became warm, and precipitation of pyridinium chloride commenced. The mixture was then placed in a refrigerator for 48 h, the resulting solid then added to a suspension of crushed ice in 1 M HCl, and the mixture extracted several times with ether. The combined ether extracts were washed successively with 1 M HCl, saturated $NaHCO_3$, and water, all at 0 °C, and dried over $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator, affording the brosylates as viscous oils which slowly solidified at −5 to −10 °C. The *cis*-brosylates **1c** and **2c** were crystallized twice from pentane before use. The brosylates were stored at −5 to −10 °C since decomposition begins in a matter of hours at room temperature.

Brosylate **1c**: mp 62–63.5 °C dec; NMR δ 0.86 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.90 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.0–2.1 (overlapping multiplets 8 H), 4.50 (m, 1 H, C2 H), 7.69 (s, 4 H, aromatic H's); IR (CH_2Cl_2) 1171, 1182, 1348, 1383 cm^{-1} ($-SO_2-$).

Brosylate **2c**: mp 76.0 °C dec; NMR δ 0.77 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.82 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.2–2.3 (overlapping multiplets, 8 H), 4.72 (m, 1 H, C2 H), 7.70 (s, 4 H, aromatic H's); IR (CH_2Cl_2) 1170, 1178, 1348, 1376 cm^{-1} ($-SO_2-$).

The *trans*-brosylate mixture of composition 46% **3c** + 54% **4c** was obtained as a semisolid: IR (CH_2Cl_2) 1182, 1351, 1379 cm^{-1} ($-SO_2-$). The *trans*-brosylate mixture of composition 88% **3c** + 12% **4c** was also obtained as a semisolid. These products were not crystallized in order not to change their compositions.

Synthesis of 5,6-Dimethyl-*exo*-2-norbornyl Acetates (1b, 2b, 3b, and 4b). The following procedure was used to convert the alcohols **1a–4a** to their acetates. To a solution of 1.0 g (0.0071 mol) of alcohol in 8 mL of anhydrous pyridine was added 4.0 mL (ca. 0.039 mol) of distilled acetic anhydride, and the solution was allowed to stand for 12 h at room temperature. The solution was then added to 120 mL of cold, saturated $NaHCO_3$ and extracted with six 50-mL portions of pentane. The combined extracts were washed successively with 2 M HCl, saturated $NaHCO_3$, and distilled water, dried over K_2CO_3, and filtered. Most of the pentane was removed by careful fractional distillation, and the pure acetates were isolated as clear liquids from the acetate-rich residue by using preparative GC.

Acetate **1b**: NMR δ 0.85 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.89 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.1–1.9 (series of multiplets, 8 H), 1.91 (s, 3 H, acetate CH_3), 4.58 (m, 1 H, C2 H); IR (neat) 1239, 1742 cm^{-1} (acetate). MS Calcd for $C_{11}H_{18}O_2$: M^+ m/e 182.1307. Found: M^+ m/e 182.1312.

Acetate **2b**: NMR δ 0.83 (d, $J \approx 7$ Hz, 3 H, CH_3), 0.91 (d, $J \approx 7$ Hz, 3 H, CH_3), 1.0–2.4 (overlapping multiplets, 11 H, including s at 1.91, 3 H, acetate CH_3), 4.90 (m, 1 H, C2 H); IR (neat) 1742, 1247 cm^{-1} (acetate). MS Calcd for $C_{11}H_{18}O_2$: M^+ m/e 182.1307. Found: M^+ m/e 182.1316.

Acetate **3b**: NMR δ 0.94 (overlapping doublets, 6 H, CH_3's), 1.0–2.2 (series of multiplets, 11 H, including s at 1.90, 3 H, acetate CH_3), 4.48 (m, 1 H, C2 H); IR (neat) 1236, 1736 cm^{-1} (acetate). MS Calcd for $C_{11}H_{18}O_2$: M^+ m/e 182.1307. Found: M^+ m/e 182.1301.

Acetate **4b**: NMR δ 0.8–2.2 (overlapping multiplets, 17 H, including s at 1.91, 3 H, acetate CH_3), 4.90 (m, 1 H, C2 H); IR

(28) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 98 (1928).
(29) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).
(30) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **514**, 197 (1934).
(31) K. Alder and W. Roth, *Chem. Ber.*, **87**, 161 (1954).
(32) E. M. Marvell, J. L. Stephenson, and J. Ong, *J. Am. Chem. Soc.*, **87**, 1267 (1965).

(CCl_4) 1241, 1736 cm^{-1} (acetate). MS Calcd for $C_{11}H_{18}O_2$: M^+ *m/e* 182.1307. Found: M^+ *m/e* 182.1312.

Product Runs. The brosylate acetolyses were conducted in anhydrous acetic acid containing 0.20 M sodium acetate, 0.20 M urea, or no solute. A solution of 3.0 g of brosylate in 83.5 mL of solvent (0.10 M) was placed in a stoppered flask in a constant-temperature bath maintained at 40.00 ± 0.05 °C. After a measured period of time (Tables I and II) the solution was added to 1 L of water in a 2-L separatory funnel and extracted with seven 100-mL portions of pentane. The combined extracts were washed three times with saturated $NaHCO_3$ and three times with water and dried over anhydrous K_2CO_3. The solution was filtered, most of the pentane removed by careful distillation through a fractionating column, and the residue analyzed by GC. In the acetic acid additions, 1.0 g of olefin and 50 mL of anhydrous acetic acid (0.16 M) were placed in a 100-mL round-bottom flask containing a magnetic stirring bar. Two drops of concentrated H_2SO_4 (ca. 1.5×10^{-2} M) were added, and the stoppered flask was immersed in a constant-temperature bath maintained at 60 ± 1 °C. After being stirred for a measured period of time (8–30 h), the mixture was added to 1 L of ice–water and the product isolated and analyzed as described for the brosylate acetolyses.

Preparative and Analytical Gas Chromatography. Product isolation utilized a Wilkens Aerograph Model A-90-P3 gas chromatograph equipped with a thermal conductivity detector and a 50 ft × $^1/_4$ in. 5% LAC 2-R-446 on 60/80 mesh acid-washed Chromosorb G column (supplied by Wilkens Instrument and Research Inc.) at an operating temperature of 150 °C and a helium flow rate of 86–100 cm^3 min^{-1}. Samples were collected in 3-mm Pyrex U-tubes immersed in a dry ice bath. The tertiary acetates are extremely prone to decomposition under these conditions, and their isolation required prior treatment of the column with ammonia. The purity of the products was checked by analytical GC. The products were characterized (identified, in the case of **1b**, **3b**, and **4b**) by means of their IR, NMR, and mass spectra. Average retention times (min) under the conditions of the GC product isolations were **7** (10.3), **16** (13.4), **6** (14.0), **17** (14.3), **5** (14.6), **11** (61.0), **8** (66.1), **12** (69.1), **4b** (72.0), **9** (73.9), **3b** (81.5), **2b** (103.0), and **1b** (105.9). Analyses of product mixtures were carried out with a Wilkens Aerograph Model 600-D gas chromatograph equipped with a flame-ionization detector and a 15 ft × $^1/_8$ in. 5% LAC 2-R-446 on 100/120 mesh acid-washed Chromosorb G column (Wilkens) at an operating temperature of 130 °C and a nitrogen flow rate of 10 cm^3 min^{-1}. Analyses are based on peak areas corrected for differences in detector response between the acetate and olefin products. Average retention times (min) under the conditions of the GC analyses were **7** (2.5), **16** (2.9), **6** (2.9), **17** (3.1), **5** (3.2), **11** (15.4), **8** (16.4), **12** (17.6), **4b** (18.0), **9** (18.8), **3b** (20.0), **2b** (27.0), and **1b** (28.4).

Product Spectral Data. β-Santenyl Acetate (8):[12] NMR δ 0.98 (d, $J \approx 7$ Hz, 3 H, 7-CH_3), 1.00 (s, 3 H, 1-CH_3), 1.1–2.0 (overlapping multiplets, 8 H), 1.94 (s, 3 H, acetate CH_3), 4.58 (distorted t with additional fine splitting, 1 H, C2 H); IR (CCl_4) 2985, 2874, 1733, 1456, 1445, 1372, 1364, 1351, 1295, 1259 (sh), 1233, 1174, 1163, 1107, 1059, 1048, 1029, 1009, 976, 943 cm^{-1}. MS Calcd for $C_{11}H_{18}O_2$: M^+ *m/e* 182.1307. Found: M^+ *m/e* 182.1307.

α-Santenyl Acetate (9):[12] NMR δ 0.82 (d, $J \approx 7$ Hz, 3 H, 7-CH_3), 0.93 (s, 3 H, 1-CH_3), 1.0–2.0 (overlapping multiplets, 8 H), 1.94 (s, 3 H, acetate CH_3), 4.71 (2 d, $J \approx 7$ and 3 Hz, 1 H, C2 H); IR (neat) 2994, 2915, 1733, 1466, 1441, 1366, 1344, 1285, 1272, 1259, 1232, 1200 (sh), 1183, 1172, 1134, 1099, 1075, 1062, 1041, 1019, 1010, 976 cm^{-1}. MS Calcd for $C_{11}H_{18}O_2$: M^+ *m/e* 182.1307. Found: M^+ *m/e* 182.1308.

***endo*-2,*exo*-3-Dimethyl-*exo*-2-norbornyl Acetate (11):** NMR δ 0.99 (d, $J \approx 7$ Hz, 3 H, 3-CH_3), 1.1–1.9 (overlapping multiplets, 8 H), 1.51 (s, 3 H, 2-CH_3), 1.89 (s, 3 H, acetate CH_3), 2.97 (b s, 1 H, C1 H); IR (CCl_4) 2994, 1727, 1686 (sh), 1468 (sh), 1447, 1431, 1357, 1314, 1300, 1284, 1279, 1242, 1218, 1206, 1192, 1125, 1099, 1074, 1050, 1030, 1009, 966 cm^{-1}.

2,3-*cis*-*endo*-Dimethyl-*exo*-2-norbornyl Acetate (12): NMR δ 0.99 (d, $J \approx 7$ Hz, 3 H, 3-CH_3), 1.1–1.9 (overlapping multiplets, 8 H), 1.33 (s, 3 H, 2-CH_3), 1.89 (s, 3 H, acetate CH_3), 2.34 (b s, 1 H, C1 H); IR (CCl_4) 2994, 2915, 1730, 1473, 1445, 1368, 1355, 1290, 1277, 1245, 1222, 1212, 1189, 1174, 1156, 1133, 1115, 1096, 1075, 1050, 1032, 1014 cm^{-1}.

***exo*-Isosantene (15):** NMR δ 0.97 (d, $J \approx 7$ Hz, 3 H, 3-CH_3), 1.1–1.9 (overlapping multiplets, 7 H), 1.98 (b s, 1 H, C4 H), 2.66 (b s, 1 H, C1 H), 4.53 and 4.80 (b s, 2 H, $=CH_2$); IR (neat) 3115, 3003, 2915, 1664, 1468, 1451, 1441, 1366, 897, 876 cm^{-1}. MS Calcd for C_9H_{14}: M^+ *m/e* 122.1095. Found: M^+ *m/e* 122.1088.

***endo*-Isosantene (16):** NMR δ 1.02 (d, $J \approx 7$ Hz, 3 H, 3-CH_3), 1.1–1.9 (overlapping multiplets, 7 H), 2.15 (b s, 1 H, C4 H), 2.64 (b s, 1 H, C1 H), 4.50 and 4.75 (b s, 2 H, $=CH_2$); IR (CCl_4) 3115, 2976, 2907, 1656, 1466, 1437, 1406, 1359, 1109, 1095, 1038, 1014, 894, 874, 861 cm^{-1}. MS Calcd for C_9H_{14}: M^+ *m/e* 122.1095. Found: M^+ *m/e* 122.1085.

Kinetic Measurements. A 100-mL volume of a 0.03 M solution of brosylate in anhydrous acetic acid containing 0.02 M excess acetic anhydride was placed in a constant-temperature bath at 25.0 °C. The progress of the reaction was followed by periodic withdrawal of 5-mL aliquots, quenching by addition to 10 mL of dioxane, and titration with standard 0.03 M sodium acetate in anhydrous acetic acid with bromophenol blue indicator. The calculations are based on 11–15 titers (V_t) covering 2–3 half-lives and an infinity titer (V_∞), the average of three measurements after at least 10 half-lives. Infinity titers were in good agreement with the theoretical volume. Rate constants for norbornyl brosylate and **1c** were obtained from the least-squares slopes of plots of log ($V_\infty - V_t$) vs. time. With **2c**, plots of log ($V_\infty - V_t$) vs. time showed regular curvature, corresponding to an increase in rate with increasing extent of reaction. The solvolytic-rearrangement pathway in Scheme I leads to eq 1 where γ is the fraction of the

$$\gamma = 1 + \frac{1}{k_X - k_N - k_R}[k_R e^{-k_X t} + (k_N - k_X)e^{-(k_N + k_R)t}] \quad (1)$$

total brosylate which has solvolyzed after time *t*, and the rate constants are defined in Scheme I. With the measured rate constant for **1c** (k_X), k_N and k_R were systematically varied to minimize $\sum(\gamma_{calcd} - \gamma_{exptl})^2$ where γ_{calcd} and γ_{exptl} are the $\sum(\gamma_{calcd} - \gamma_{exptl})^2$ calculated and experimental values of γ at time *t*. The minimization was carried out with a Hewlett-Packard Model 67 programmable calculator. The experimental values of γ from three separate sets of rate data were reproduced to average deviations of ±0.56, ±0.76, and ±0.93% by eq 1 using the best fit values of k_N and k_R. The average best fit values of k_N and k_R are listed in Table III. The rate constant for **3c** and the maximum rate constant for **4c** were estimated from the initial rates for the 46:54 and 88:12 mixtures of **3c** and **4c**.

Acknowledgment. Financial assistance from E. I. du Pont de Nemours and Co., the Koppers Co., the National Science Foundation, and the National Research Council of Canada is gratefully acknowledged. We thank Mr. Daniel Krezenski for technical assistance.

Registry No. **1a**, 60362-81-4; **1a** acid phthalate, 71185-67-6; **1b**, 71214-44-3; **1c**, 71185-68-7; **2a**, 54339-25-2; **2a** acid phthalate, 71214-45-4; **2b**, 71185-69-8; **2c**, 71214-46-5; **3a**, 60322-68-1; **3a** acid phthalate, 71214-47-6; **3b**, 60322-75-0; **3c**, 71214-48-7; **4a**, 60338-43-4; **4a** acid phthalate, 71214-49-8; **4b**, 60322-74-9; **4c**, 71214-50-1; **5**, 37459-99-7; **6**, 695-79-4; **7**, 695-80-7; **8**, 60426-40-6; **9**, 60426-39-3; **11**, 71185-70-1; **12**, 71214-51-2; **15**, 529-15-7; **16**, 529-14-6; **17**, 497-35-8; maleic anhydride, 108-31-6; cyclopentadiene, 542-92-7; 5-norbornene-*endo*-2,3-dicarboxylic anhydride, 129-64-6; 5-norbornene-*exo*-2,3-dicarboxylic anhydride, 2746-19-2; fumaryl chloride, 627-63-4; 5-norbornene-*trans*-2,3-dicarboxylic acid chloride, 4582-21-2; *cis*-*exo*-5,6-bis(hydroxymethyl)norbornene, 699-95-6; *cis*-*endo*-5,6-bis(hydroxymethyl)norbornene, 699-97-8; *trans*-5,6-bis(hydroxymethyl)norbornene, 699-96-7; *cis*-*exo*-5,6-bis(hydroxymethyl)norbornene ditosylate, 70096-09-2; *cis*-*endo*-5,6-bis(hydroxymethyl)-norbornene ditosylate, 70116-05-1; *trans*-5,6-bis(hydroxymethyl)-norbornene ditosylate, 38339-47-8.