Acetolysis of [n.3.2]Propellane Tosylates

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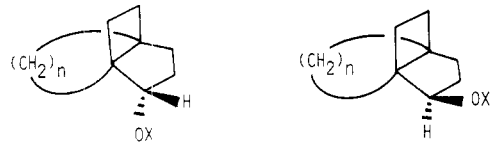
Acetolysis of [*n*.3.2]propellane tosylates **1a–d** and **2a–d** was studied in order to elucidate the steric effect of the third rings in these systems on the acetolysis rates and to synthesize 1,7-methylene-bridged norbornane skeletons. It was found that, in contrast with the case of exo tosylates, the acetolysis rates of endo ones were greatly affected by the nature (rigid or flexible) of the third rings. While the steric deceleration observed for *endo*-[3.3.2]propellane (**1a**) was explained in terms of steric hindrance to ionization due to a fairly rigid nature of the third ring, i.e., cyclopentane, the steric acceleration found for *endo*-[5.3.2]- and *endo*-[6.3.2]propellane (**1c** and **1d**) was attributed to nonbonded strain in the ground state which might be relieved by ionization without steric strain in the transition state, owing to the flexible nature of the third rings, i.e., cycloheptane and cyclooctane. In most cases, the rearrangement products such as olefins **7a–d** and alcohols **9a–d**, having 1,7-methylene-bridged norbornane skeletons, which were derived from 1,2-migration of the cyclobutane bond, were obtained in good yields.

It has been well-known that the acetolysis rates of arenesulfonates are subject to steric acceleration or steric deceleration depending on whether the transition state is less or more crowded than the ground state,[1,2] and the steric effect can quantitatively be related to the differences in nonbonded strains in the ground and transition states ($GS_{strain} - TS_{strain}$).[3] Generally, in the cases of acyclic and flexible alicyclic systems, solvolysis rates of sterically more crowded compounds are enhanced because of relief of GS_{strain} by the departure of the leaving group.[1] On the other hand, with rigid U-shaped bi- and tricyclic systems such as *endo*-2-norbornyl and *endo*-5,6-trimethylene-*endo*-8-norbornyl tosylates, remarkable steric deceleration is observed due to an increase of TS_{strain} by steric hindrance to ionization.[2]

We have previously described the significant effect of the third rings (five- to eight-membered alicyclic rings) on the stereoselectivity in the hydride reduction of [*n*.3.2]-propellanones[4a] and on the rates of the chromic acid oxidation of [*n*.3.2]propellanols,[4b] which was attributed to the steric effect associated with the conformational rigidity or flexibility of the ring systems. From the above studies, it appeared that the [*n*.3.2]propellane framework might serve as a good model for examination of the steric effect of common and medium sized alicyclic rings conjoined in polycyclic systems.

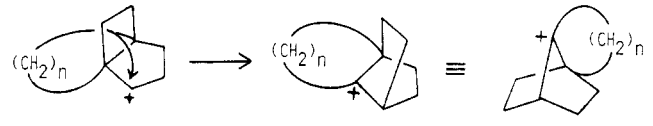
In this connection, we wish to report here on the acetolysis of *endo*- and *exo*-[*n*.3.2]propellane tosylates (endo, **1a–d**; exo, **2a–d**) where either steric acceleration or deceleration is expected, especially in a series of endo tosylates, depending on the conformational rigidity or the flexibility of the third rings. At the same time, from a synthetic point of view, it is notable that 1,2-alkyl migration of the cyclobutane bond of [*n*.3.2]propellanes by the acetolysis results in the formation of 1,7-methylene-bridged norbornanes whose derivatives are of much interest in view of the adamantane rearrangement of tricyclodecanes ($n = 3$)[5a] and tricycloundecanes ($n = 4$).[5b]



1 a-d X=Ts
3 a-d X=H

2 a-d X=Ts
4 a-d X=H

a, n=3; b, n=4; c, n=5; d, n=6



Results and Discussion

endo- and *exo*-propellane tosylates **1a–d** and **2a–d** were prepared from the corresponding alcohols (**3a–d** and **4a–d**)[4] in the usual manner. From the ^1H NMR study of the methine proton geminal to the OTs group, it was pointed out that both the endo and the exo isomers were in the boat conformation, with a slight difference in the degree of folding of the cyclopentane envelope; the proton of the endo tosylates appeared as two doublets (J = 2.0, 4.0 Hz) or a single doublet (J = 2.9–3.3 Hz) and that of the exo isomers as two doublets (J = 7.0, 9.5 Hz) or a triplet (J = 8.0 Hz).[4,6] The rates of sodium acetate buffered acetolysis of **1a–d** and **2a–d** were measured by the usual titration method, and each reaction showed good first-order kinetics. The kinetic results are summarized in Table I along with the calculated rates of the *endo*- and *exo*-bicyclo[3.2.0]hept-2-yl tosylate (**5** and **6**). Since it has been reported that the solvolysis rate of *exo*-**5** exceeds that of *endo*-**6** by a factor of 100 due to anchimeric assistance by the cyclobutane bond[7] and, moreover, that the σ participation is relatively insensitive to the conformational change

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(2) (a) Brown, H. C.; Rothberg, I.; Schleyer, P. v. R.; Donaldson, M. M.; Harper, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 1653. (b) Brown, H. C. *Tetrahedron* **1976**, *22*, 179.
(3) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1964**, *86*, 1854.
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Table I. Kinetic Data for Acetolysis of 1a-d and 2a-d

compd[a]	T,[b] °C	k,[c] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}[d]
1a	60.0	$(3.72 \pm 0.06) \times 10^{-4}$	23.9	−2.7	
	50.0	$(1.29 \pm 0.03) \times 10^{-4}$			
	40.0	$(3.25 \pm 0.06) \times 10^{-5}$			
	25[e]	4.79×10^{-6}			42 (0.45)
1b	60.0	$(1.44 \pm 0.02) \times 10^{-3}$	27.1	9.5	
	50.0	$(4.71 \pm 0.10) \times 10^{-4}$			
	40.0	$(9.17 \pm 0.16) \times 10^{-5}$			
	25[e]	1.02×10^{-5}			90 (0.95)
1c	25.0	$(5.58 \pm 0.08) \times 10^{-4}$			4900 (52)
1d	25.0	$(1.12 \pm 0.11) \times 10^{-3}$			9900 (100)
5	25[f]	1.07×10^{-5}			95 (1.0)
2a	90.0	$(2.95 \pm 0.08) \times 10^{-4}$			
	75.0	$(6.27 \pm 0.10) \times 10^{-5}$			
	60.0	$(1.01 \pm 0.01) \times 10^{-5}$	22.6	−13.3	
	25[e]	2.09×10^{-7}			1.8
2b	90.0	$(1.16 \pm 0.01) \times 10^{-3}$			
	75.0	$(2.42 \pm 0.03) \times 10^{-4}$			
	60.0	$(4.87 \pm 0.09) \times 10^{-5}$	21.1	−14.8	
	25[e]	1.25×10^{-6}			11
2c	90.0	$(1.97 \pm 0.03) \times 10^{-4}$			
	75.0	$(3.82 \pm 0.01) \times 10^{-5}$			
	60.0	$(8.27 \pm 0.06) \times 10^{-6}$	21.2	−17.3	
	25[e]	2.02×10^{-7}			1.8
2d	90.0	$(6.85 \pm 0.12) \times 10^{-4}$			
	75.0	$(1.24 \pm 0.06) \times 10^{-4}$			
	60.0	$(2.26 \pm 0.10) \times 10^{-5}$	22.8	−11.2	
	25[e]	4.32×10^{-7}			3.8
6	25[f]	1.13×10^{-7}			1.0

[a] Compound is 0.04 M in acetic acid buffered with 0.08 M sodium acetate. [b] Temperatures are ±0.1 °C. [c] The errors are deviations from the average of at least two runs. [d] Relative rates to that of 6 at 25 °C. Relative rates to that of 5 are given in parentheses. [e] Extrapolated value. [f] Calculated from the data on the corresponding brosylate at 50 °C[7] by using a factor of 3 to relate the relative reactivities[9] and the average $\Delta H^{\ddagger}$ value of 22 kcal/mol found for 2a-d.

of the bicyclo[3.2.0]heptane moiety,[8] it is reasonable to expect a similar degree of acceleration due to σ participation in *endo*-**1a–d** compared with that for the corresponding *exo*-**2a–d**. It is also reasonable to consider the relative rates of *endo*-**1a–d** and *exo*-**2a–d** in terms of steric effect on ionization in comparison with the rates of *exo*-**5** and *endo*-**6**, respectively.

The most significant feature of the results shown in Table I is that, in a series of endo isomers, the rates of *endo*-[5.3.2]- and *endo*-[6.3.2]propellane (**1c** and **1d**) were considerably enhanced compared with the model compound **5** (52 and 100 times as large as that of **5**, respectively), although the rates of [3.3.2]- and [4.3.2]propellane (**1a** and **1b**) were half of and comparable with that of **5**, respectively. The acetolysis rates of these tricyclic systems are expected to be enhanced in comparison with that of **5** because of an increase in GS_{strain} due to nonbonded interaction between the *endo*-tosyl group and the third alicyclic ring, which is absent in the uncrowded bicyclic molecule **5**. Moreover, in the cases of **1c** and **1d**, relief of GS_{strain} may be achieved by ionization without considerable TS_{strain} as in the cases of flexible molecules,[1] since the flexibility of the third ring, i.e., cycloheptane and cyclooctane, reduces unfavorable steric repulsion between the leaving group and the third ring in the transition state. Consequently, the accelerated rates of **1c** and **1d** may be ascribed mainly to an increase in GS_{strain}. On the other hand, the rate deceleration observed for **1a** may be considered as the result of an increase in TS_{strain} arising from steric hindrance to ionization by the fairly rigid third ring, i.e., cyclopentane, as in the cases of rigid U-shaped molecules.[2] In contrast, the relative rates of *exo*-**2a**, **-2c**, and **-2d** were only 2–4 times that of the model compound **6**. The small rate enhancement may be due to relief of nonbonded strain around the endo hydrogen geminal to the OTs group by ionization. But the rate of *exo*-[4.3.2]propellane (**2b**) was unusually large (k_{rel} = 11). The reason for the unexpected kinetic result as well as that for the exceptional behavior in product formation remains uncertain.

Table II. Product Distribution for Acetolysis of 1a-d and 2a-d

compd	product, %[a] 7	8	9	3	4	other[b]
1a	54	<1	2	44		
1b	39		9	48		4
1c	68		3	28		1
1d	68		3	20	5	4
2a	5	2	9		84	
2b	44	5	28		10	7, 6
2c	43	1	6		39	11
2d	56	1	4		26	8, 5

[a] After reduction of the crude acetolysis products with lithium aluminum hydride. [b] Unidentified alcohol.

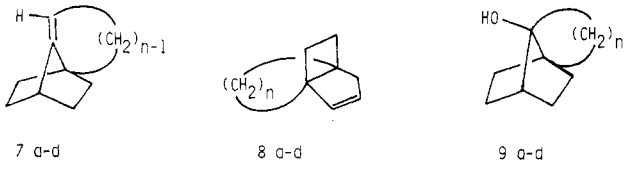
The product distribution of the acetolysis of the tosylates is shown in Table II. Since identification of the acetate products was difficult because of their poor resolution on GLC, they were identified after reduction with lithium aluminum hydride to the corresponding alcohols which were easily resoluble. Total recovery of materials, including all of the olefins and alcohols, ranged from 73 to 85%.

Structural assignments for the rearranged olefins **7a–d** were based on the ^{13}C NMR data and the results of the

(8) The rate of acetolysis was enhanced only 5 times as the conformation changed from boat to planar. Yano, K.; Isobe, M.; Yoshida, K. *J. Am. Chem. Soc.* **1978**, *100*, 6166. In the present case, the conformational change is small, as indicated by the ^1H NMR study, and, therefore, the degree of σ participation may be thought to be comparable to that of the cases of 5 and 6.

(9) Cooke, B. J. A.; Story, P. R. *J. Org. Chem.* **1975**, *40*, 2656.

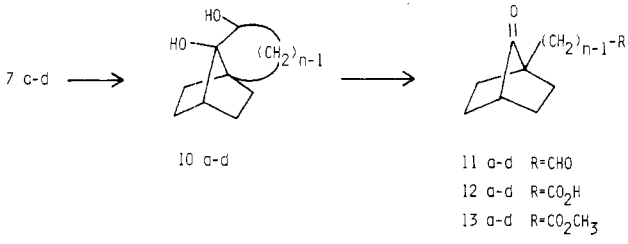
degradations described below, along with the spectral and analytical properties. The ^{13}C NMR spectra of **7a–d** ex-



7 a-d 8 a-d 9 a-d

a, n=3; b, n=4; c, n=5; d, n=6

hibited a quaternary and a tertiary olefinic carbon and two pairs of secondary carbons which had twice the intensity of other methylene carbons, indicating the presence of symmetry in **7a–d** (see Experimental Section). Oxidation of **7a–d** with osmium tetroxide gave the diols **10a–d** (78–83%), the subsequent cleavage with lead tetraacetate led to the formation of the keto aldehydes **11a–d** (95–99%), and then bromine–water oxidation of **11a–d** afforded the keto acids **12a–d** (86–90%) which were converted into the keto esters **13a–d** with diazomethane. All of **11a–d**, **12a–d**, and **13a–d** showed distinctive carbonyl



10 a-d

11 a-d R=CHO
12 a-d R=CO_2H
13 a-d R=CO_2CH_3

a, n=3; b, n=4; c, n=5; d, n=6

frequencies at 1760 cm^{-1}, characteristic of the 7-norbornanone skeleton.[6a,10] These results are consistent with the assigned structures of **7a–d**. The unrearranged olefins **8a–d** were confirmed by their identity with authentic samples prepared from the reaction of the respective propellanone tosylhydrazones **14a–d** with methyllithium. The structures of the rearranged alcohols **9a–d** were established by the conversion of the alcohols into the olefins **7a–d** by dehydration with thionyl chloride–pyridine.

As shown in Table II, in most cases, the rearranged olefins **7a–d**, having 1,7-methylene-bridged norbornane skeletons, were obtained as major products, along with a small amounts of the rearranged alcohols **9a–d**. The product distributions were not independent of the size of the third rings and the exo or endo configuration of the tosyl group of the starting materials; however, it seems difficult at present to elucidate a wholly realistic explanation of the observed difference in products. Nevertheless, the following points should be noted. As well as the kinetic results, the facts that (i) the relative ratios of the rearranged products to the unrearranged ones were slightly larger in the case of endo tosylates than in the case of the exo ones except for **2b**, (ii) the unrearranged olefins **8a–d** were not formed in the cases of endo tosylates, and (iii) the configuration of the OTs group in endo tosylates was almost retained in the unrearranged alcohols **3a–d** suggest the operation of σ participation of the cyclobutane bond in endo tosylates. The unrearranged alcohols **4a–d** derived from *exo*-**2a–d** also retained the original configuration of the starting materials. This may be accounted by extremely stereoselective capture of a classical ion from the exo side of the propellane systems.

(10) Cargill, R. L.; Beckham, M. E.; Damewood, J. R.; Pond, D. M.; Bundy, W. A. *J. Org. Chem.* **1972**, *37*, 78.

In conclusion, the kinetic study of the acetolysis of *endo*-**1a–d** demonstrates that the acetolysis rates were decelerated due to steric hindrance to ionization or accelerated due to relief of GS_{strain}, depending on the nature (rigid or flexible) of the third ring in these systems. Moreover, the rearrangement products through 1,2-migration of the cyclobutane bond were obtained in good yields and may serve as important precursors of adamantanoids. A study on the further rearrangement of the obtainable products is in progress and will be reported shortly.

Experimental Section[11]

[n.3.2]Propellane Tosylates 1a–d and 2a–d. The tosylates **1a–d** and **2a–d** were prepared in 60–80% yields from the corresponding [n.3.2]propellanols **3a–d** and **4a–d**[4] in the usual manner by treatment with tosyl chloride in pyridine followed by aqueous workup. The endo tosylates **1b–d** would not crystallize, though spectral analyses indicated that they were sufficiently pure. These were subsequently used in the kinetic and preparative runs without further purification. The other tosylates were recrystallized from petroleum ether.

1a: mp 69–70 °C; IR 1590, 1350, 1160, 905, 870 cm^{-1}; ^1H NMR δ 1.00–2.30 (m, 14 H), 2.42 (s, 3 H), 4.45 (2 d, J = 2.0, 4.0 Hz, 1 H), 7.22, 7.66 (2 d, J = 8.0 Hz, 4 H). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24; S, 10.46. Found: C, 66.68; H, 7.38; S, 10.28.

1b: IR 1590, 1350, 1165, 875 cm^{-1}; ^1H NMR δ 1.00–2.20 (m, 16 H), 2.42 (s, 3 H), 4.50 (2 d, J = 2.0, 4.0 Hz, 1 H), 7.24, 7.69 (2 d, J = 8.0 Hz, 4 H).

1c: IR 1595, 1350, 1165, 875 cm^{-1}; ^1H NMR δ 1.00–2.30 (m, 18 H), 2.43 (s, 3 H), 4.35 (d, J = 3.3 Hz, 1 H), 7.25, 7.69 (2 d, J = 8.0 Hz, 4 H).

1d: IR 1595, 1350, 1165, 880, 850 cm^{-1}; ^1H NMR δ 1.00–2.40 (m, 20 H), 2.43 (s, 3 H), 4.00 (d, J = 2.9 Hz, 1 H), 7.25, 7.69 (2 d, J = 8.0 Hz, 4 H).

2a: mp 61–62 °C; IR 1595, 1350, 1165, 950, 900, 805 cm^{-1}; ^1H NMR δ 1.00–2.40 (m, 14 H), 2.43 (s, 3 H), 4.38 (2 d, J = 9.5, 7.0 Hz, 1 H), 7.23, 7.65 (2 d, J = 8.0 Hz, 4 H). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24; S, 10.46. Found: C, 66.48; H, 7.30; S, 10.63.

2b: mp 53–54 °C; IR 1595, 1350, 1165, 960, 900, 825 cm^{-1}; ^1H NMR δ 1.00–2.20 (m, 16 H), 2.43 (s, 3 H), 4.39 (t, J = 8.0 Hz, 1 H), 7.24, 7.68 (2 d, J = 8, 0 Hz, 4 H). Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55; S, 10.01. Found: C, 67.38; H, 7.64; S, 10.20.

2c: mp 69–70 °C; IR 1595, 1350, 1165, 960, 895 cm^{-1}; ^1H NMR δ 1.00–2.20 (m, 18 H), 2.43 (s, 3 H), 4.48 (t, J = 8.0 Hz, 1 H), 7.24, 7.69 (2 d, J = 8.0 Hz, 4 H). Anal. Calcd for $C_{19}H_{26}O_3S$: C, 68.23; H, 7.84; S, 9.59. Found: C, 68.13; H, 7.97; S, 9.41.

2d: mp 67–69 °C; IR 1595, 1350, 1165, 950, 890, 875 cm^{-1}; ^1H NMR δ 1.00–2.30 (m, 20 H), 2.44 (s, 3 H), 4.78 (t, J = 8.0 Hz, 1 H), 7.25, 7.70 (2 d, J = 8.0 Hz, 4 H). Anal. Calcd for $C_{20}H_{28}O_3S$: C, 68.93; H, 8.10; S, 9.20. Found: C, 68.82; H, 8.26; S, 9.27.

Kinetic Measurements. The acetic acid solvent was heated at reflux with acetic anhydride for 24 h and distilled. For the removal of traces of water, 5% of acetic anhydride was added. The solutions of tosylates (0.04 M) in acetic acid containing sodium acetate (0.08 M) were heated at the indicated temperature, and aliquots were removed at appropriate intervals and cooled. Titration was carried out with 0.0209 M perchloric acid in acetic acid which was standardized against the sodium acetate solution by using bromophenol blue indicator. Rate constants were determined by the infinity-titer method. The results are summarized in Table I and are the average of at least duplicate measurements.

Preparative Acetolysis of the Tosylates 1a–d and 2a–d. The solutions of **1a–d** and **2a–d** in anhydrous acetic acid containing a twofold molar excess of sodium acetate were heated for

(11) Melting points are uncorrected. Infrared spectra were recorded by using a JASCO IR-G spectrometer. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4 solutions and ^{13}C NMR spectra on a JEOL JNM-FX-60S spectrometer in $CDCl_3$ solutions. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC separation was conducted on a Varian Aerograph 90-P chromatograph using columns A, 10% FFAP, and B, 5% SE-30.

more than 10 half-lives. The solutions were diluted with water and extracted with ether, and the ether extracts were washed with sodium carbonate solution and water and then dried over anhydrous sodium sulfate. After removal of the ether, the volatile products were distilled under reduced pressure and analyzed by GLC (column A). Since identification of the acetate products was difficult because of their poor resolution on GLC, they were reduced to the corresponding alcohols which afforded improved separation. The solutions of the distillates of the acetolysis products in ether were added dropwise to a suspension of a large excess of lithium aluminum hydride in ether, and the mixtures were stirred at room temperature for 1 h. Water and 1 N hydrochloric acid were added, and the ethereal solutions were washed with sodium carbonate solution and water and then dried (Na_2SO_4). After evaporation of the ether the products were analyzed by GLC (columns A and B) and separated by preparative GLC (column A). The total yields of the products amounted to 73–85%. The distribution of the products is summarized in Table II.

The unrearranged alcohols **3a–d** and **4a–d** were identified with the authentic materials by comparison of IR and ^1H NMR spectra and GLC retention times, and the unrearranged olefins **8a–d** were determined by comparing GLC retention times with the samples alternatively prepared as described below. The structures of the rearranged olefins **7a–d** and alcohols **9a–d** were established by some degradations along with the spectral and analytical data.

7a: IR 3050, 825, 805 cm^{-1}; MS *m/e* (relative intensity) 134 (85, M^+), 119 (52), 106 (90), 105 (100), 91 (97); ^1H NMR δ 1.10–2.10 (m, 10 H), 2.42 (t, J = 4 Hz, 1 H), 2.64–2.90 (m, 2 H), 4.77 (t, J = 2 Hz, 1 H); ^{13}C NMR δ 27.8 (t), 32.9 (t, 2 C), 33.4 (d), 34.1 (t, 2 C), 39.7 (t), 59.2 (s), 107.1 (d), 158.3 (s). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.44; H, 10.54.

7b: IR 3050, 850, 800 cm^{-1}; MS *m/e* (relative intensity) 148 (62, M^+), 120 (100), 119 (98), 92 (60), 91 (83); ^1H NMR δ 1.20–2.10 (m, 14 H), 2.32 (t, J = 3.5 Hz, 1 H), 5.29 (t, J = 4 Hz, 1 H); ^{13}C NMR δ 21.2 (t), 24.9 (t), 30.1 (t), 30.4 (t, 2 C), 35.0 (t, 2 C), 39.0 (d), 40.9 (s), 108.7 (d), 150.5 (s). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.11; H, 10.96.

7c: IR 3050, 835, 800 cm^{-1}; MS *m/e* (relative intensity) 162 (38, M^+), 134 (100), 133 (65), 91 (68); ^1H NMR δ 1.20–2.00 (m, 14 H), 2.00–2.30 (m, 3 H), 5.12 (t, J = 4 Hz, 1 H); ^{13}C NMR δ 24.6 (t), 29.7 (t), 29.9 (t), 30.2 (t, 2 C), 35.6 (t), 36.9 (t, 2 C), 44.3 (d), 46.0 (s), 112.9 (d), 150.9 (s). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.36.

7d: IR 3050, 830, 805 cm^{-1}; MS *m/e* (relative intensity) 176 (48, M^+), 148 (100), 147 (58), 133 (58), 91 (75); ^1H NMR δ 1.00–2.40 (m, 19 H), 5.02 (t, J = 8 Hz, 1 H); ^{13}C NMR δ 22.2 (t), 24.5 (t), 25.5 (t), 27.3 (t), 29.0 (t, 2 C), 29.4 (t), 34.9 (t, 2 C), 42.8 (d), 46.1 (s), 108.3 (d), 154.3 (s). Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.54; H, 11.58.

9a: mp 59–60 °C; IR 3400, 1100, 1020, 990, 890 cm^{-1}; MS *m/e* (relative intensity) 152 (17, M^+), 134 (41), 98 (100); ^1H NMR δ 0.90–2.00 (m); ^{13}C NMR δ 26.1 (t), 26.5 (t), 28.5 (t, 2 C), 29.2 (t), 33.9 (t), 36.2 (t), 39.8 (d), 58.7 (s), 97.5 (s). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.65; H, 10.57.

9b: mp 101–102 °C; IR 3450, 1160, 1135, 1075, 990 cm^{-1}; MS *m/e* (relative intensity) 166 (34, M^+), 148 (15), 111 (100); ^1H NMR δ 1.00–2.20 (m); ^{13}C NMR δ 21.1 (t), 21.3 (t), 26.2 (t), 27.1 (t), 28.3 (t), 29.2 (t), 30.0 (t), 35.2 (t), 44.2 (d), 44.9 (s), 82.2 (s). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.12; H, 10.89.

9c: mp 39–41 °C; IR 3450, 1110, 1090, 1040, 1010, 935, 880 cm^{-1}; MS *m/e* (relative intensity) 180 (60, M^+), 162 (85), 125 (95), 91 (100); ^1H NMR δ 1.00–2.30 (m). Anal. Calcd for $C_{12}H_{20}O$: C, 79.74; H, 11.18. Found: C, 79.70; H, 11.30.

9d: mp 37–39 °C; IR 3400, 1110, 1055, 1000, 940, 880 cm^{-1}; MS *m/e* (relative intensity) 194 (25, M^+), 176 (63), 96 (100); ^1H NMR δ 0.90–2.30 (m). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.20; H, 11.57.

Along with the above products small amounts of unidentified alcohols were obtained in the cases of **1b–d** and **2b–d**. **1b** gave unidentified A (4%) and **2b** gave A (7%) and B (6%). A: IR 3400, 1120, 1070 cm^{-1}; MS *m/e* (relative intensity) 166 (10, M^+), 138 (100), 109 (44). B: IR 3400, 1070, 970, 940 cm^{-1}; MS *m/e* (relative intensity) 166 (81, M^+), 138 (100). Both **1c** and **2c** gave unidentified C (1 and 11%, respectively). C: IR 3400, 1150, 1050 cm^{-1}; MS *m/e* (relative intensity) 180 (23, M^+), 162 (12), 137 (100). **1d** gave unidentified D (4%) and **2d** gave D (8%) and E (5%). D: IR 3450, 1150, 1000 cm^{-1}; MS *m/e* (relative intensity) 194 (6, M^+), 165 (44), 151 (100). E: IR 3400, 1040, 990 cm^{-1}; MS *m/e* (relative intensity) 194 (19, M^+), 176 (59), 166 (47), 148 (100), 147 (90).

Alternative Preparation of the Olefins 8a–d. The solutions of [*n*.3.2]propellanones and tosylhydrazine (1.3-fold excess) in methanol were heated under gentle reflux for 3 h and cooled to room temperature. The tosylhydrazones **14a–d** were collected (57–70%) and recrystallized from methanol. **14a–d** showed IR absorptions at 3200, 1640, 1590, 1320, and 1150 cm^{-1}.

14a: mp 173–175 °C dec. Anal. Calcd for $C_{17}H_{22}O_2N_2S$: C, 64.12; H, 6.96; N, 8.80; S, 10.07. Found: C, 64.09; H, 6.87; N, 8.71; S, 10.08.

14b: mp 174–175 °C dec. Anal. Calcd for $C_{18}H_{24}O_2N_2S$: C, 65.03; H, 7.28; N, 8.43; S, 9.64. Found: C, 64.99; H, 7.24; N, 8.37; S, 9.55.

14c: mp 165–167 °C dec. Anal. Calcd for $C_{19}H_{26}O_2N_2S$: C, 65.86; H, 7.56; N, 8.09; S, 9.25. Found: C, 65.88; H, 7.63; N, 8.10; S, 9.21.

14d: mp 182–183 °C dec. Anal. Calcd for $C_{20}H_{28}O_2N_2S$: C, 66.63; H, 7.83; N, 7.77; S, 8.89. Found: C, 66.50; H, 7.93; N, 7.77; S, 8.94.

To the solutions of **14a–d** in ether was added dropwise 1 N methyllithium in ether (1.5-fold excess), and the mixtures were stirred at room temperature for 8 h. Water was added carefully, and the ethereal solutions were washed with water and dried (Na_2SO_4). After evaporation of the ether, distillation gave **8a–d** (53–60%) as colorless liquids which were purified by preparative GLC (column B).

8a: IR 3050, 725 cm^{-1}; MS *m/e* (relative intensity) 134 (2, M^+), 106 (100); ^1H NMR δ 1.00–2.00 (m, 10 H), 2.35 (mc, 2 H), 5.50–5.76 (m, 2 H). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.63; H, 10.66.

8b: IR 3050, 715 cm^{-1}; MS *m/e* (relative intensity) 148 (1, M^+), 120 (100); ^1H NMR δ 0.90–2.30 (m, 14 H), 5.63 (br s, 2 H). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.06; H, 11.03.

8c: IR 3050, 715 cm^{-1}; MS *m/e* (relative intensity) 162 (1, M^+), 134 (100); ^1H NMR δ 0.80–2.20 (m, 15 H), 2.52 (d, J = 16 Hz, 1 H), 5.30–5.50 (m, 1 H), 5.60–5.80 (m, 1 H). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.49; H, 11.47.

8d: IR 3050, 720 cm^{-1}; MS *m/e* (relative intensity) 176 (1, M^+), 148 (100); ^1H NMR δ 0.80–2.10 (m, 17 H), 2.72 (d, J = 16 Hz, 1 H), 5.50–5.75 (m, 2 H). Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.49; H, 11.43.

Degradation of the Olefins 7a–d. The solutions of **7a–d** (1.5 mmol) and osmium tetroxide (1.7 mmol) in 10 mL of pyridine were stirred in the dark at room temperature for 30 h. To the resulting brown solutions was added a solution of sodium bisulfite (6 mmol) in 15 mL of water and 7.5 mL of pyridine, and the mixtures were stirred for 12 h and extracted with chloroform. The chloroform extracts were washed with 1 N hydrochloric acid and water and dried (K_2CO_3). Evaporation of the solvent gave the diols **10a–d** as brown solids (78–83%). **10a**: IR 3350, 1120, 1075, 1055, 1045 cm^{-1}. **10b**: IR 3350, 1110, 1055, 990 cm^{-1}. **10c**: IR 3350, 1110, 1030, 980 cm^{-1}. **10d**: IR 3350, 1100, 1020 cm^{-1}.

To the solution of the crude diols in 20 mL of benzene was added dropwise a solution of a 1.1-fold excess of lead tetraacetate in 15 mL of benzene, and the mixtures were stirred at room temperature for 1 h. After filtration, the solvent was evaporated to afford the crude keto aldehydes **11a–d** (95–99%) as pale yellow oils, which showed carbonyl absorptions in their IR spectra at 1760 and 1715 cm^{-1}.

To the above aldehydes was added a large excess of saturated bromine–water, and the mixtures were stirred for 30 min. Water and sodium bisulfite solution were added and the mixture was extracted with ether. The ethereal solutions were washed with water and dried (Na_2SO_4). Evaporation of the solvent gave the keto acids **12a–d** (86–90%), which showed carbonyl absorptions at 1760 and 1700 cm^{-1}.

The keto acids **12a–d** were treated with ethereal diazomethane to afford the keto esters **13a–d**, which showed IR absorptions at 1760, 1730, 1165 cm^{-1}. Semicarbazones were prepared in the usual manner and recrystallized from ethanol.

13a: MS *m/e* (relative intensity) 196 (6, M^+), 168 (72), 165 (45), 136 (77), 94 (100); ^1H NMR δ 1.40–2.10 (m, 11 H), 2.25 (t,

J = 7 Hz, 2 H), 3.59 (s, 3 H); semicarbazone, mp 187–188 °C. Anal. Calcd for $C_{12}H_{19}O_3N_3$: C, 56.90; H, 7.56; N, 16.59. Found: C, 56.66; H, 7.58; N, 16.39.

13b: MS m/e (relative intensity) 210 (5, M^+), 182 (45), 179 (27), 150 (66), 108 (100), 93 (52); ^1H NMR δ 1.20–2.12 (m, 13 H), 2.24 (t, J = 7 Hz, 2 H), 3.59 (s, 3 H); semicarbazone, mp 169–170 °C. Anal. Calcd for $C_{13}H_{21}O_3N_3$: C, 58.41; H, 7.92; N, 15.72. Found: C, 58.26; H, 7.92; N, 15.69.

13c: MS m/e (relative intensity) 224 (22, M^+), 196 (25), 193 (22), 164 (63), 122 (69), 95 (91), 81 (100); ^1H NMR δ 1.00–2.05 (m, 15 H), 2.25 (t, J = 7 Hz, 2 H), 3.59 (s, 3 H); semicarbazone, mp 200–201 °C. Anal. Calcd for $C_{14}H_{23}O_3N_3$: C, 59.76; H, 8.24; N, 14.94. Found: C, 59.65; H, 8.26; N, 15.08.

13d: MS m/e (relative intensity) 238 (30, M^+), 207 (21), 178 (24), 95 (94), 81 (100); ^1H NMR δ 1.00–2.10 (m, 17 H), 2.22 (t, J = 7 Hz, 2 H), 3.58 (s, 3 H); semicarbazone, mp 184–185 °C. Anal. Calcd for $C_{15}H_{25}O_3N_3$: C, 60.99; H, 8.53; N, 14.23. Found: C, 60.81; H, 8.67; N, 14.32.

Dehydration of the Alcohols 9a–d. To the solutions of **9a–d** in pyridine and methylene chloride (1:3) was added dropwise a 1.5 molar excess of thionyl chloride with stirring at 0 °C, and the solutions were stirred for 30 min at 0 °C and for 4 h at room temperature. The solutions were poured into ice–water, the organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined extracts were washed with 1 N hydrochloric acid, sodium carbonate solution, and water and dried over calcium chloride. Evaporation of the solvent followed by distillation gave the olefins **7a–d** (71–80%), which were identical with the sample obtained by acetolysis of the tosylates **1a–d** and **2a–d** (^1H NMR spectra and GLC retention times).

Registry No. 1a, 72378-11-1; **1b**, 72390-09-1; **1c**, 72378-12-2; **1d**, 72378-13-3; **2a**, 72402-28-9; **2b**, 72441-81-7; **2c**, 72402-29-0; **2d**, 72402-30-3; **3a**, 68457-30-7; **3b**, 68457-31-8; **3c**, 68457-32-9; **3d**, 68457-33-0; **4a**, 68509-83-1; **4b**, 68509-84-2; **4c**, 68509-85-3; **4d**, 68509-86-4; **5**, 72378-14-4; **6**, 72402-31-4; **7a**, 72378-15-5; **7b**, 72390-10-4; **7c**, 72378-16-6; **7d**, 72378-17-7; **8a**, 72378-18-8; **8b**, 72378-19-9; **8c**, 72378-20-2; **8d**, 72378-21-3; **9a**, 72378-22-4; **9b**, 72378-23-5; **9c**, 72378-24-6; **9d**, 72378-25-7; **10a**, 72378-26-8; **10b**, 72378-27-9; **10c**, 72378-28-0; **10d**, 72378-29-1; **11a**, 72378-30-4; **11b**, 72378-31-5; **11c**, 72378-32-6; **11d**, 72378-33-7; **12a**, 72378-34-8; **12b**, 72378-35-9; **12c**, 72378-36-0; **12d**, 72378-37-1; **13a**, 72378-38-2; **13a** semicarbazone, 72378-39-3; **13b**, 72378-40-6; **13b** semicarbazone, 72378-41-7; **13c**, 72378-42-8; **13c** semicarbazone, 72378-43-9; **13d**, 72378-44-0; **13d** semicarbazone, 72378-45-1; **14a**, 72378-73-5; **14b**, 72378-74-6; **14c**, 72378-75-7; **14d**, 72378-76-8.

Special Salt Effect upon the Products of the Acetolysis of 1-Phenylpropyl 2-Tosylate

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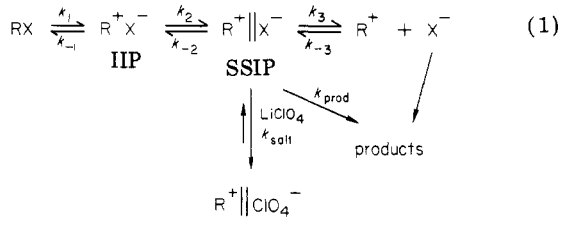
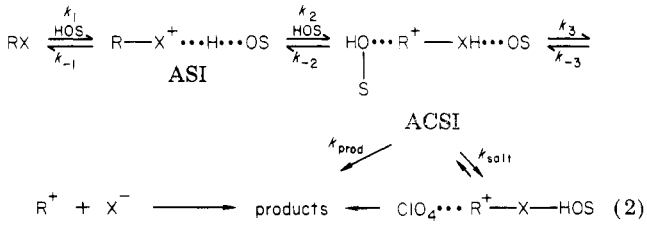
Addition of increasing amounts lithium perchlorate to the acetolysis of optically active 1-phenylpropyl 2-tosylate causes an initial rapid increase in the proportion of retained (k_Δ) acetate produced by phenyl assistance. When more than 0.02 M $LiClO_4$ is added, no further changes in the proportion of retained acetate are observed. This result is believed to be the first reported "special-salt" effect upon product distribution. The results are interpreted in terms of a common first intermediate for the two competing (solvent- and aryl-assisted) pathways rather than for two completely independent competing reactions.

The special-salt effect upon the rates of solvolysis reactions was originally reported by Winstein et al.[1] and has since been observed in several other systems.[2] This effect is manifested by a large slope of rate vs. salt concentration for lower rather than higher concentrations of "special salt". The accepted explanation for this phenomenon has been that the solvent-separated ion pair (SSIP)[1] is intercepted by the nonnucleophilic anion of the special salt to form a new ion pair (reaction 1). However, Winstein's



essentially kinetic evidence did not define the geometries of the two intermediates, the intimate ion pair (IIP) and the solvent-separated ion pair (SSIP), that he proposed.[1] An equivalent explanation using an alternative reaction scheme has recently been proposed by Dannenberg.[3] This explanation is a result of an interpretation of reaction paths for nucleophilic substitution reactions calculated by using molecular orbital theory, which defines, within limits, the geometry of these intermediates. In this scheme, the anion–cation-stabilized intermediate (ACSI) is trapped as indicated in reaction 2. We shall refer to the more recent



scheme in the discussion that follows. Both of these schemes involve trapping of the second intermediate along the reaction path to complete dissociation. The mani-

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(3) J. J. Dannenberg, *J. Am. Chem. Soc.*, 98, 6261 (1976).

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