Cyclopropyl Solvolyses. III. Parent Cyclopropyl Derivatives and Methyl-Substituted Cyclopropyl Tosylates[1]

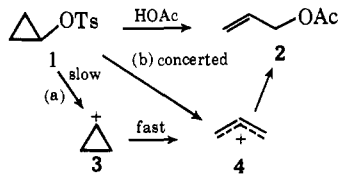
P. v. R. Schleyer,* [2a] W. F. Sliwinski,[2a,3] G. W. Van Dine,[2a,4] U. Schöllkopf,[2b] J. Paust,[2b] and K. Fellenberger[2b]

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540, and Organisch-Chemisches Institut der Universität Göttingen, 34 Göttingen, Germany.
Received April 22, 1971

Abstract: Acetolysis results for the various β-methyl-substituted cyclopropyl tosylates are reported. The kinetic results are correlated with a treatment based on electronic and steric effects in ground and transition states, assuming stereospecific ring opening according to the Woodward-Hoffmann-DePuy predictions and considerable progress toward allyl cations in the transition states. The results of the standard mechanistic criteria [m value, $(k_{\text{aq alc}}/k_{\text{AcOH}})_Y$, $k_{\text{OTs}}/k_{\text{Br}}$, and α-methyl/hydrogen rate ratio] for the parent cyclopropyl system indicate that solvolysis is a concerted k_Δ process. The magnitude of anchimeric assistance in the cyclopropyl system is estimated by two independent means to be at least a factor of 10^4–10^5 in rate at 25°.

The relative inertness of the cyclopropyl system toward nucleophilic substitution was first noted by Gustavson in 1891.[5] Sixty years later Brown, *et al.*,[6] explained this inertness on the basis of "I strain," the unfavorable increase in bond angle strain in going from the ground state to the transition state. The solvolysis of a cyclopropyl derivative was finally achieved by Roberts and Chambers.[7] Acetolysis of cyclopropyl tosylate (**1**), 10^5 slower in rate than that of cyclohexyl tosylate, gave allyl acetate (**2**) as the only product isolated. Based on this slow rate of acetolysis, Roberts and Chambers proposed a two-step mechanism: slow ionization to a cyclopropyl cation (**3**) followed by a fast opening of **3** to the allyl cation (**4**) (Scheme I, path a). This interpretation was questioned in 1961 by Schleyer and Nicholas,[8] who pointed out that the rate of acetolysis of **1** was actually faster than that of 7-norbornyl tosylate (Figure 1), despite the larger angle at the reaction site of the latter. This comparison suggested that the rate of solvolysis of cyclopropyl tosylate was enhanced,[9] and that ionization and ring opening were concerted.

Scheme I



Subsequently, the mechanism of ring opening in carbonium ion reactions of cyclopropyl derivatives has received widespread attention. The transformation of a cyclopropyl cation to an allyl cation has been elegantly treated as an electrocyclic ring opening[10] and predicted to be stereospecific and "disrotatory." Following a suggestion by DePuy,[11] the extended Hückel calculations of Woodward and Hoffmann further predicted that the direction of *concerted* ring opening should depend on the stereochemistry of the leaving group,[10a] groups cis to the leaving group rotating inwards. These predictions have been confirmed by more recent theoretical calculations[12] and have received widespread experimental support,[1a,b,11b,13–15] based chiefly on in-

(1) Previous papers: (a) I, P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, 88, 2868 (1966); (b) II, U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967). Reviews: (c) P. v. R. Schleyer, 20th National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 1967, Abstracts, pp 5–19; (d) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, 7, 588 (1968); *Angew. Chem.*, 80, 603 (1968). A detailed review will be published by P. v. R. Schleyer, W. Sliwinski, and T. Su in "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y. For a preliminary version of this review see: (e) T. M. Su, Ph.D. Thesis, Princeton University, 1970.

(2) (a) Princeton University; (b) University of Göttingen.

(3) Ph.D. Thesis, Princeton University, 1971; National Science Foundation Fellow, 1965–1967; American Machine and Foundry Fellow, 1967–1969.

(4) Ph.D. Thesis, Princeton University, 1967; American Machine and Foundry Fellow, 1963–1964.

(5) G. Gustavson, *J. Prakt. Chem.*, [2] 43, 396 (1891).

(6) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, 73, 212 (1951); see also H. C. Brown and M. Gerstein, *ibid.*, 72, 2926 (1950).

(7) J. D. Roberts and V. C. Chambers, *ibid.*, 73, 5034 (1951).

(8) P. v. R. Schleyer and R. D. Nicholas, *ibid.*, 83, 182 (1961).

(9) This was later put on a more quantitative basis: (a) C. S. Foote, *ibid.*, 86, 1853 (1964); (b) P. v. R. Schleyer, *ibid.*, 86, 1854, 1856 (1964).

(10) (a) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

(11) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, W. Germany, 1970, p 46; (b) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, 87, 4006 (1965).

(12) (a) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967); (b) W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 6, 813 (1967); (c) D. T. Clark and G. Smale, *Tetrahedron*, 25, 13 (1969); (d) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 13, 365 (1969); (e) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 93, 4290, 4291, 4292 (1971); (f) L. Radom, J. Pople, and P. v. R. Schleyer, to be published.

(13) (a) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Amer. Chem. Soc.*, 87, 4007 (1965); (b) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, 88, 3343 (1966); (c) J. W. Hausser and N. J. Pinkowski, *ibid.*, 89, 6981 (1967); (d) J. W. Hausser and M. J. Grubber, private communication; *cf.* M. J. Grubber, Ph.D. Thesis, Duquesne University, 1968; (e) P. S. Skell and S. R. Sandler, *J. Amer. Chem. Soc.*, 80, 2024 (1958); (f) S. R. Sandler, *J. Org. Chem.*, 32, 3876 (1967); (g) L. Skattebol, *ibid.*, 31, 1554 (1966); (h) G. H. Whitham and M.

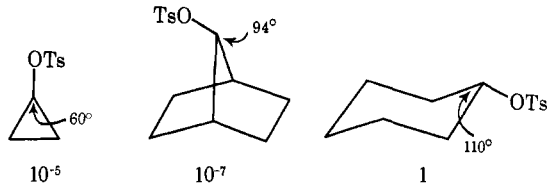
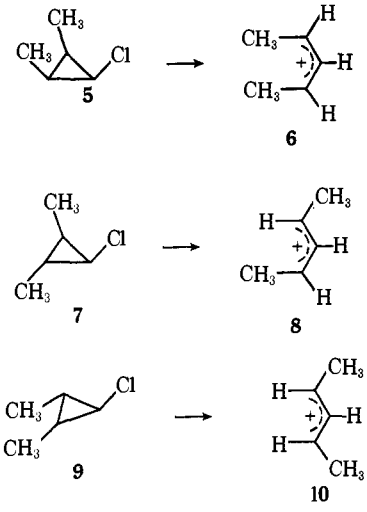


Figure 1. Relative acetolysis rates and bond angles.

direct kinetic evidence from cyclopropyl solvolyses[1a,b,11b,13] and thermolyses.[14] In direct experimental verification of the original predictions,[10a] the isomeric 2,3-dimethylcyclopropyl chlorides (**5**, **7**, and **9**) ionize in strong acid media (SbF_5, SO_2ClF at $-100°$) to yield the stereoisomeric allyl cations (**6**, **8**, and **10**).[15]

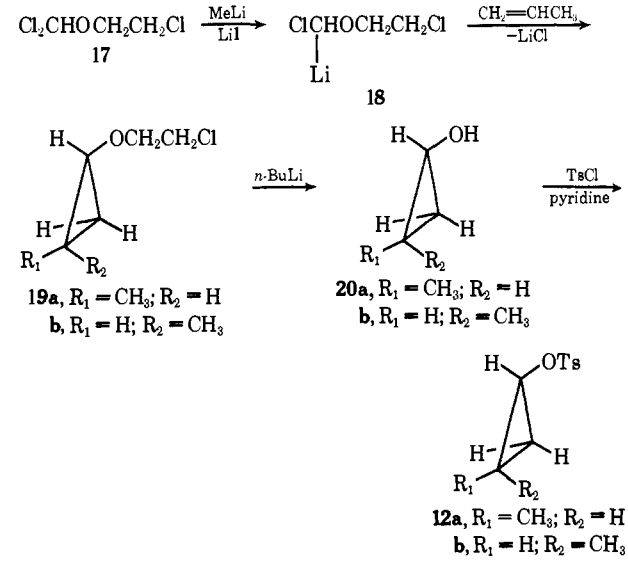


Among the earliest solvolytic evidence for concerted ring opening was our preliminary communication[1a] dealing with the acetolysis of a number of substituted cyclopropyl tosylates. The present paper presents a detailed study of the solvolysis of parent cyclopropyl derivatives, as well as the rate effects of methyl substitution in cyclopropyl tosylate. The companion manuscript will deal with the effects of various alkyl substituents and of changes in the leaving group.[16] The behavior of polycyclic systems[1b] will be considered in full subsequently.

Results

Cyclopropanol (**11**), prepared by the method of Magrane and Cottle[17] as modified by DePuy, *et al.*,[18] was converted into a number of sulfonate ester derivatives (**1**, **13–15**). Cyclopropyl bromide (**16**) was commercially available (Aldrich). Alkyl-substituted cyclopropyl tosylates were made by the method described previously,[19] as shown in Scheme II, for the preparation

Scheme II



of 2-methylcyclopropyl tosylate (**12**). The key step in this procedure, carbene or carbenoid addition to the desired olefin, requires the presence of some LiI in the methyllithium used (see Experimental Section). Addition to olefins not possessing a C_2 symmetry axis perpendicular to the plane of the double bond gives a mixture of isomers with the cis isomer predominating. For 2-methylcyclopropyl tosylate (**12**) the isomers were separated by preparative glpc as the β-chloroethyl ethers (**19**). For the tosylate mixtures **21** and **22** resulting from carbene addition to *cis*-2-butene and 2-methyl-2-butene, respectively, partial solvolysis allowed determination of the faster rate and recovery of the slower isomer in pure form. Stereochemical assignments of cyclopropyl derivatives are based on the magnitude of the vicinal coupling constants of the distinctive α proton resonances in the nmr spectra ($J_{cis} > J_{trans}$).[20]

Kinetic studies were carried out titrimetrically using the sealed ampoule technique. The method of Winstein[21] was employed for tosylate acetolyses. Cyclopropyl bromide (**16**) was acetolyzed in anhydrous acetic acid buffered with a slight excess of sodium acetate. Solvolyses of **16** were followed by Volhard titrations for liberated bromide.[22] For tosylate solvolyses carried

Wright, *Chem. Commun.*, 294 (1967); (i) J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, **33**, 1173 (1968); (j) D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969); (k) D. T. Clark and G. Smale, *Chem. Commun.*, 868 (1969); (l) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 924 (1967); (m) W. E. Parham and K. S. Yong, *ibid.*, **33**, 3947 (1968); (n) W. E. Parham and K. S. Yong, *ibid.*, **35**, 683 (1970).

(14) (a) C. W. Jefford and R. Medary, *Tetrahedron Lett.*, 2069 (1966); (b) C. W. Jefford, E. Huang-Yen, and R. Medary, *ibid.*, 6317 (1966); (c) C. W. Jefford and W. Wojnarowski, *ibid.*, 199 (1968); (d) T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *ibid.*, 1123 (1967); (e) T. Ando, H. Yamanaka, and W. Funasaka, *ibid.*, 2587 (1967); (f) R. Fields, R. N. Haszeldine, and D. Peter, *Chem. Commun.*, 1081 (1967); (g) L. Ghosez, P. Laroche, and G. Slinckx, *Tetrahedron Lett.*, 2767 (1967); (h) L. Ghosez, G. Slinckx, M. Glineur, P. Hoot, and P. Laroche, *ibid.*, 2773 (1967); (i) G. C. Robinson, *J. Org. Chem.*, **32**, 3218 (1967); (j) W. E. Parham, F. M. Parham, J. F. Dooley, and M. K. Meilahn, *ibid.*, **33**, 3651 (1968); (k) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 1379 (1967); (l) M. S. Baird, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc. C*, 1173 (1969); M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969); (n) M. S. Baird and C. B. Reese, *J. Chem. Soc. C*, 1803, 1809 (1969).

(15) P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

(16) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).

(17) J. K. Magrane and D. L. Cottle, *ibid.*, **64**, 484 (1942).

(18) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).

(19) U. Schöllkopf, J. Paust, A. Al-Azrak, and H. Schumacher, *Chem. Ber.*, **99**, 3391 (1966).

(20) (a) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962); (b) S. Meiboom and L. C. Snyder, *ibid.*, **89**, 1038 (1967); for a theoretical treatment see: M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(21) S. Winstein, C. Hansen, and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 812 (1948).

(22) H. Laitinen, "Chemical Analysis," McGraw-Hill, New York, N. Y., 1960, p 214.

Table I. Rates of Solvolysis of Parent Cyclopropyl Derivatives

Compd	c-C_3H_5X, X =	Solvent	Temp °C	k_1,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	OTs	HOAc	150.0	$(8.17 \pm 0.01) \times 10^{-6}$	32.3	−6.1
			185.0	$(1.67 \pm 0.02) \times 10^{-4}$		
			100.0[b]	4.16×10^{-8}		
			25.0[b]	5.71×10^{-13}		
		50% EtOH	124.6	$(1.04 \pm 0.04) \times 10^{-5}$	29.3	−8.3
			150.2	$(1.03 \pm 0.05) \times 10^{-4}$		
			100.0[b]	8.44×10^{-7}		
			25.0[b]	3.29×10^{-11}		
		80% EtOH	150.1	$(1.827 \pm 0.006) \times 10^{-5}$	29.7	−10.7
			175.0	$(1.377 \pm 0.003) \times 10^{-4}$		
			100.0[b]	1.40×10^{-7}		
			25.0[b]	4.71×10^{-12}		
13	ONs[c]	HOAc	150.0	$(8.58 \pm 0.01) \times 10^{-5}$	28.8	−9.7
			175.0	$(6.15 \pm 0.05) \times 10^{-4}$		
			100.0[b]	7.66×10^{-7}		
			25.0[b]	3.47×10^{-11}		
14	ODNs[d]	HOAc	124.9	$(1.24 \pm 0.01) \times 10^{-4}$	30.8	0.4
			149.6	$(1.28 \pm 0.01) \times 10^{-3}$		
			100.0[b]	8.61×10^{-6}		
			25.0[b]	1.98×10^{-10}		
15	OTf[e]	HOAc	75.15	$(3.01 \pm 0.07) \times 10^{-5}$	26.3	−4.1
			100.1	$(4.07 \pm 0.04) \times 10^{-4}$		
			100.0[b]	4.04×10^{-4}		
			25.0[b]	4.35×10^{-8}		
		50% EtOH	50.4	$(8.46 \pm 0.06) \times 10^{-5}$	23.2	−5.7
			78.1	$(1.58 \pm 0.04) \times 10^{-3}$		
			100.0[b]	1.18×10^{-2}		
			25.0[b]	3.60×10^{-6}		
		80% EtOH	78.1	$(2.77 \pm 0.02) \times 10^{-4}$	23.2	−9.2
			100.6	$(2.17 \pm 0.08) \times 10^{-3}$		
			100.0[b]	2.06×10^{-3}		
			25.0[b]	6.40×10^{-7}		
16	Br	HOAc[f]	174.9	$(3.17 \pm 0.02) \times 10^{-6}$	33.0	−10.8
			200.0	$(2.39 \pm 0.04) \times 10^{-5}$		
			100.0[b]	1.55×10^{-9}		
			25.0[b]	1.69×10^{-14}		
		50% EtOH	139.1	$(9.87 \pm 0.02) \times 10^{-6}$	29.0	−11.7
			162.8	$(7.16 \pm 0.24) \times 10^{-5}$		
			100.0[b]	2.19×10^{-7}		
			25.0[b]	9.30×10^{-12}		
		80% EtOH	160.0	$(5.54 \pm 0.04) \times 10^{-6}$	28.2	−18.1
			180.0	$(2.47 \pm 0.01) \times 10^{-5}$		
			100.0[b]	2.44×10^{-8}		
			25.0[b]	1.34×10^{-12}		

[a] Average deviation of two or more kinetic determinations. [b] Calculated from data at other temperatures. [c] *p*-Nitrobenzenesulfonate ester. [d] 2,4-Dinitrobenzenesulfonate ester. [e] Trifluoromethanesulfonate (triflate) ester; all kinetics on this compound were carried out conductometrically. [f] Buffered with 0.032 *M* NaOAc; substrate concentration 0.025–0.03 *M*.

out in aqueous solvents, the liberated acid was determined by titration with standard base. Rate constants and activation parameters were determined using least squares computer programs and are summarized in Tables I and II.

Methyl-Substituted Cyclopropyl Tosylates. The relative acetolysis rates at 100° for the various methyl-substituted cyclopropyl tosylates are given in the third column of Table III. It is easily seen that the kinetic results are at least qualitatively consistent with concerted, stereospecific ring opening according to the Woodward–Hoffmann–DePuy rules. Thus, the isomeric 2,3-dimethylcyclopropyl tosylates show the expected order of reactivity, k_{21a} (38,000) > k_{23} (460) > k_{21b} (2.2), based on the known stabilities of the allyl cations, **10** > **8** > **6**.[15] If a classical cyclopropyl cation were formed as the first intermediate, ground state strain relief[22a] would be expected to be the predominating factor affecting relative reactivity and the opposite order of reactivity ($k_{21b} > k_{23} > k_{21a}$) would be predicted. The same argument applies to the observed reactivities ($k_{trans} > k_{cis}$) for the isomers of tosylates **12** and **22**. This same order of reactivity ($k_{trans} > k_{cis}$) has been reported for derivatives of the 2-phenylcyclopropyl system.[13b-d]

The magnitudes of α- and β-methyl substituent effects also indicate extensive charge delocalization in the solvolysis transition state. At 25° in acetic acid, 1-methylcyclopropyl tosylate (**24**) solvolyzes only 1080 times faster than cyclopropyl tosylate (**1**).[23] This is much smaller acceleration than the factor of at least 10^6 and probably 10^8 expected for carbonium ion behavior;[24] since there is no involvement of external

(22a) NOTE ADDED IN PROOF. For X-ray evidence of steric crowding in cis-trisubstituted cyclopropanes, see W. Saenger and C. H. Schwalbe, *J. Org. Chem.*, **36**, 3401 (1971).

(23) The effect of 1-methyl substitution in cyclopropyl bromide is similarly only a factor of 40 increase in rate (130°, 50% EtOH): E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, 83, 2719 (1961).

(24) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 72; (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

Table II. Rates of Acetolysis of Methyl-Substituted Cyclopropyl Tosylates[a]

Compd	Substituents	Temp, °C	k_1, sec^{-1} [b]	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
12a	*trans*-2-Methyl	125.0	$(7.70 \pm 0.10) \times 10^{-5}$	29.9	−2.9
		150.0	$(7.61 \pm 0.04) \times 10^{-4}$		
		100.0[c]	5.76×10^{-6}		
		25.0[c]	1.83×10^{-10}		
12b	*cis*-2-Methyl	150.0	$(3.60 \pm 0.09) \times 10^{-5}$	30.8	−6.7
		175.0	$(2.95 \pm 0.08) \times 10^{-4}$		
		100.0[c]	2.33×10^{-7}		
		25.0[c]	5.32×10^{-12}		
21a	*trans,trans*-2,3-Dimethyl	75.0	$(1.06 \pm 0.10) \times 10^{-4}$	27.3	1.2
		100.0	$(1.59 \pm 0.15) \times 10^{-3}$		
		25.0[c]	1.23×10^{-7}		
21b	*cis,cis*-2,3-Dimethyl	150.0	$(3.13 \pm 0.02) \times 10^{-5}$	35.9	5.0
		170.3	$(2.31 \pm 0.04) \times 10^{-4}$		
		100.0[c]	9.01×10^{-8}		
		25.0[c]	3.68×10^{-13}		
22a	*trans*-2,2,3-Trimethyl	75.0	$(1.28 \pm 0.10) \times 10^{-4}$	26.9	0.7
		100.0	$(1.86 \pm 0.15) \times 10^{-3}$		
		25.0[c]	1.61×10^{-7}		
22b	*cis*-2,2,3-Trimethyl	124.9	$(5.035 \pm 0.004) \times 10^{-5}$	31.0	−0.8
		149.9	$(5.44 \pm 0.03) \times 10^{-4}$		
		100.0[c]	3.44×10^{-6}		
		25.0[c]	7.35×10^{-11}		
23	*cis,trans*-2,3-Dimethyl	100.1	$(1.95 \pm 0.02) \times 10^{-5}$	29.8	−0.7
		124.5	$(2.45 \pm 0.09) \times 10^{-4}$		
		100.0[c]	1.93×10^{-5}		
		25.0[c]	6.23×10^{-10}		
24	1-Methyl	100.1	$(1.302 \pm 0.002) \times 10^{-5}$	28.7	−4.6
		125.0	$(1.465 \pm 0.005) \times 10^{-4}$		
		150.0	$(1.423 \pm 0.004) \times 10^{-3}$		
		25.0[c]	6.16×10^{-10}		
27	2,2,3,3-Tetramethyl	75.0	$(1.61 \pm 0.04) \times 10^{-5}$	29.8	4.9
		100.0	$(3.10 \pm 0.03) \times 10^{-4}$		
		25.0[c]	9.99×10^{-9}		
28	2,2-Dimethyl	100.0	$(1.79 \pm 0.02) \times 10^{-5}$	30.3	0.6
		150.0	$(2.55 \pm 0.03) \times 10^{-3}$		
		25.0[c]	4.86×10^{-10}		

[a] Anhydrous acetic acid, ~0.03 *M* in substrate. [b] Average deviation of two or more kinetic determinations. [c] Calculated from data at other temperatures.

Table III. Relative Acetolysis Rates of Cyclopropyl Tosylates

Compd	Substituents	Observed k_{rel}, 100°	Calculated rates at 100° [70][a]	Calculated rates at 100° [138][b]
1	Parent	1	1	1
12b	*cis*-2-Methyl	5.7	8.0	15.8
12a	*trans*-2-Methyl	138	70	138
28	2,2-Dimethyl	430	560	2180
23	*cis,trans*-2,3-Dimethyl	460	560	2180
21b	*cis,cis*-2,3-Dimethyl	2.2	1.7	8.5
21a	*trans,trans*-2,3-Dimethyl	38,000	21,800	84,700
22b	*cis*-2,2,3-Trimethyl	83	117	900
22a	*trans*-2,2,3-Trimethyl	44,700	175,000	1,340,000
27	2,2,3,3-Tetramethyl	7450	36,500	1,240,000

[a] Based on an electronic methyl stabilization factor of 70; see text. [b] Based on an electronic methyl stabilization factor of 138.

nucleophile in the solvolysis transition state, *i.e.*, no nucleophilic solvent assistance (*vide infra*), this decreased α-methyl substitution effect must be due to internal charge delocalization.[24b] The effect of β-methyl substitution (k_{12a}/k_1 = 138 at 100° in HOAc) is also much larger than the small factor of 1–6 that would be predicted for β-methyl substitution in the absence of anchimeric assistance.[25] This factor of 138 is quite large for a β-methyl effect even in a participating system, exceeding by a factor of 2 the accelerating effect of a 1-methyl group on the rate of *exo*-2-norbornyl solvolyses.[26] In fact, when corrected for the difference in leaving groups,[27] the *trans*-β-methyl substitution effect is seen to approach the factor of 2060 (k_{26b}/k_{26a}, 100°, 99.5% aqueous HCOOH) found for γ-methyl substitution in allyl chloride (**26a**).[28]

RCH=CH—CH_2Cl

26a, R = H
b, R = CH_3

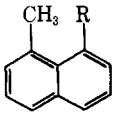
(25) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 432–433; (b) P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, 87, 5169 (1965); see also ref 24a, pp 35, 92.

(26) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 89, 3901 (1967).

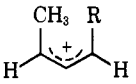
(27) The magnitude of substituent effects in the cyclopropyl system depends on the leaving group: Cl > Br > OTs.[16] The *trans*-β-methyl substitution effect for cyclopropyl chloride (**25**) can be roughly estimated as a factor of 950–1350 in acetic acid at 100°.[16]

(28) C. A. Vernon, *J. Chem. Soc.*, 423 (1954); *cf.* ref 24a, p 78.

In our preliminary communication[1a] a quantitative treatment of the rate data for various β-methyl-substituted cyclopropyl tosylates was presented assuming the acetolyses proceeded with stereospecific ring opening and with considerable progress toward open allylic cations in the transition state. The observed relative rates in Table III are accounted for quite well by this treatment, considering electronic and steric effects in ground and transition states. It was assumed originally that each β-methyl substituent contributes a constant rate enhancement factor due to electronic stabilization of the protoallylic transition state. Steric effects due to the substituents were evaluated as follows: In the ground state, the "extra" strain (above that present in cyclopropane) due to nonbonded interactions between two methyl groups and a tosyl group on the same side of the cyclopropane ring (**21b, 22b, 27**) was estimated to be 1.7 kal/mol.[22a] The ground-state strain due to two cis methyl groups was taken as 1.1 kcal/mol based on thermal isomerization data for *cis*- and *trans*-1,2-dimethylcyclopropane;[29] the ground-state strain due to a tosyl group and one cis methyl substituent (**12b, 22a, 23, 28**) was considered negligible. Transition-state strain energy differences were approximated by the strains of the open allyl cations containing as many interior methyl groups as expected for stereospecific Woodward–Hoffmann–DePuy opening (cation **6**, with two cis methyls, for **21b, 22b**, and **27**; cation **8**, with one cis methyl, for **12b, 22a, 23**, and **28**; and cation **10**, no cis methyls, for **12a** and **21a**); nonbonded strains in **6** and **8** were estimated as 7.6 and 1.6 kcal/mol, respectively, using 1,8-dimethylnaphthalene (**29a**) and 1-methylnaphthalene (**29b**) as models;[30,31] the trans, trans cation **10** was assumed to be unstrained.



29a, R = CH_3
b, R = H



6, R = CH_3
8, R = H

Assuming entropy differences to be insignificant,[32] 1.7 kcal/mol in strain energy difference between ground state and transition state is equal to a power of 10 in rate at 100°. The acetolysis rate of any tosylate in Table III relative to cyclopropyl tosylate is then given by

$$k_{rel} = (\text{electronic methyl factor})^n \times 10^{[(\text{ground-state strain} - \text{transition-state strain})/1.7]} \quad (1)$$

where n is the number of β-methyl substituents and the strain energies are in kcal/mol.

In our original communication,[1a] an electronic stabilization factor of 5000 for two β-methyl substituents was assumed, about a factor of 70 per methyl ($70.7^2 = 5000$). Using this electronic methyl factor of 70 and the estimated strain energy differences given above, the relative rates given in column two of Table III can be calculated. Thus, the relative rate of **22b** is given by eq 1 as

$$k_{rel_{22b}} = (70)^3 \times 10^{[(1.7 - 7.6)/1.7]} = 117$$

and similarly for the other compounds in Table III. Despite the many assumptions present in this treatment, the quantitative agreement with experimentally observed rates can be seen to be excellent except for **22a** and **27**, and even these calculated rates are accurate to within factors of 4 and 5, respectively. The qualitative ordering is correct in all cases except for tetrasubstituted **27**.

Originally,[1a] experimental rates for the monomethyl compounds **12a** and **12b** were not available. If our present experimental rate ratio k_{12a}/k_1 of 138 (HOAc, 100°) is taken as the electronic methyl factor and the above calculations are repeated using the same strain factors, the calculated rates given in the third column of Table III are obtained. Here the quantitative agreement with experiment is appreciably worse. The qualitative ordering, however, is still quite good; only the calculated rates for **22b** and **27** are now out of order.

The predictive shortcomings of the above calculations as applied to the highly substituted tosylates **22** and **27** appear to be primarily attributable to the incorrect assumption of a constant electronic methyl stabilization factor. It is reasonable that the net electronic stabilization per methyl should decrease somewhat with increasing methyl substitution (saturation effect); experimentally this is seen to be the case (Table IV). Thus while the rate ratio for the addition of the first *trans*-β-methyl group (k_{12a}/k_1) is 138 (HOAc, 100°), that for addition of a *trans*-β-methyl group where one β-methyl substituent is already present is ~78 (k_{23}/k_{12b}, k_{28}/k_{12b}). If two β-methyl substituents are already present, addition of another *trans*-β-methyl group produces an acceleration of only 38 in rate (k_{22b}/k_{21b}), and an even smaller effect (~25) is estimated for addition of a fourth β-methyl substituent. It is for this reason that the above treatment gives better agreement with experiment using the assumed electronic methyl factor of 70 than with the experimentally found factor of 138 for the first β-methyl substituent. Also, this is why the largest quantitative discrepancies in both cases involve the most highly substituted compounds. Other possible drawbacks in this treatment (besides neglect of entropy and errors in the assumed

Table IV. Effects of *trans*-β-Methyl Substituents; Acetolysis Rate Ratios at 100°

12a:1	138
23:12b	81
28:12b	75
22b:21b	38
27:22b	25[a]

[a] Corrected from the observed ratio of 90, which contains a factor of 3.5 for acceleration in **27** due to relief of ground state steric crowding of the two trans methyl groups at the 2 and 3 positions. This factor of 3.5 was obtained by dividing the total rate enhancement (38,000) for **21a** by the expected electronic stabilization effect ($138 \times [(81 + 75)/2] = 10{,}650$).

(29) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 122 (1960); W. D. Good, *J. Chem. Thermodyn.*, **3**, 539 (1971).

(30) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, 80, 905 (1958); *cf.* G. Suld and A. P. Stuart, *J. Org. Chem.*, **29**, 2939 (1964); D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, 64, 1723 (1960).

(31) The observed difference in reactivity (E_a) between **6** and **8** is 6.5 kcal/mol (4.4 kcal/mol in free energy),[15] in good agreement with these models.

(32) Differences in measured entropies of activation (Table II) are not insignificant, but these differences may not be meaningful. In solvolysis reactions, it is very seldom possible to interpret $\Delta S^{\ddagger}$ values in a meaningful way, since ordering of solvent as well as of substrate is involved in a complicated manner. For this reason comparison of relative rates (*i.e.*, free energies) rather than enthalpies is usually preferred.

Table V. Relative Solvolysis Rates and Mechanistic Criteria for Parent Cyclopropyl Derivatives[a]

Compd	c-C_3H_5X, X =	k_{rel}, 200° AcOH	k_{rel}, 200° 50% EtOH	k_{rel}, 25° AcOH	k_{rel}, 25° 50% EtOH	m,[b] 25°	$\left(\frac{k_{aq\ alc}}{k_{AcOH}}\right)_Y$[c]
15	OTf	1720	2460	76,000	110,000	0.454	0.91
14	ODNs[d]	134		350			
13	ONs[e]	6.8		61			
1	OTs	1[f]	1[g]	1[h]	1[h]	0.508	0.57
16	Br	0.045	0.24	0.03	0.29	0.510	1.8
25	Cl		0.03[i]				

[a] For definitions and discussion of these criteria see ref 35a and references therein. [b] Aqueous ethanol. [c] All values at 100°. [d] 2,4-Dinitrobenzenesulfonate. [e] p-Nitrobenzenesulfonate. [f] $k_1 = 5.3 \times 10^{-4}$ sec^{-1}. [g] $k_1 = 4.5 \times 10^{-3}$ sec^{-1}. [h] For absolute rates see Table I. [i] From ref 7.

strain energies), such as differences in the degree of ring opening in the various transition states and possible differences in the electronic stabilization afforded by cis and trans substituents,[12c] are considered in our companion paper.[16] Whatever the deficiencies, however, this treatment provides a solid, interpretive framework for consideration of the experimental data in Table III, and there can be little doubt about the correctness of its two basic assumptions, stereospecific, Woodward–Hoffmann ring opening and a protoallylic transition state (*i.e.*, a considerable degree of ring opening and charge delocalization to the β positions).

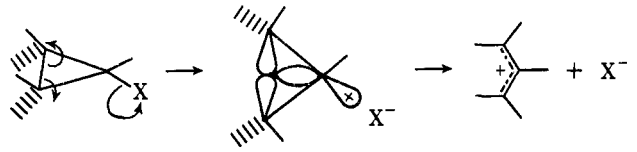


Figure 2.

Parent Cyclopropyl Derivatives and Standard Mechanistic Criteria. The cyclopropyl arenesulfonates **13** and **14** were prepared while experimenting to find a leaving group suitable for the study of some constrained cyclopropyl systems whose tosylate derivatives were not sufficiently reactive; use of the trifluoromethanesulfonate (triflate) leaving group eventually provided the solution to this problem.[33] Table V gives the relative solvolysis rates and derived standard mechanistic criteria for the various cyclopropyl derivatives studied; the extrapolated, relative solvolysis rates are given at 200° and 25° with the results in 50% aqueous ethanol and Roberts' result for cyclopropyl chloride (**30**).[7] As can be seen from Table V, the relative rates are reasonably independent of temperature.

The tosylate/bromide leaving group rate ratios for the parent cyclopropyl systems (4 to 33 depending on solvent and temperature)[34] are unusually low for secondary substrates.[35] Following prior interpretation,[35b] these low values would indicate charge delocalization in the transition state due to nucleophilic solvent participation. However, it is likely that participating systems, in which the charge is also delocalized at the transition state, should also show low OTs/Br rate ratios. Furthermore we now recognize that steric effects may detract somewhat from the mechanistic significance of OTs/Br rate ratios since secondary tosylates, but not secondary bromides, suffer from unavoidable 1,5-type ground-state steric interactions.[24b,35a,36] The reduction of this steric effect in cyclopropyl tosylate (**1**), in which the adjacent methylene groups are bent back by the ring, could thus be partly responsible for the very low k_{OTs}/k_{Br} ratios observed in this system. The other mechanistic criteria are less ambiguous.

The rate ratio $(k_{aq\ alc}/k_{AcOH})_Y$ is a measure of the sensitivity of a substrate to changes in solvent nucleophilicity.[37] The $(k_{aq\ alc}/k_{AcOH})_Y$ values in Table V are quite low, in the range normally found for carbonium ion (SN1, lim[37a,38]) processes.[35a,37b] The low magnitude of these ratios for cyclopropyl derivatives shows that there is no specific backside nucleophilic involvement of solvent in the transition states for solvolysis,[37] *i.e.*, the solvolyses of cyclopropyl derivatives are not k_s processes.[39] On the other hand, the cyclopropyl m values (Table V), which are a measure of substrate sensitivity to changes in solvent "ionizing power" (Y),[40] are much lower than would be expected for limiting (k_c) solvolysis ($m \approx 1$),[39] and they fall in the range normally found for k_s and k_Δ substrates,[35a,41] both of which benefit from charge delocalization in the transition state. These mechanistic criteria [$(k_{aq\ alc}/k_{AcOH})_Y$, m] together with the low α-methyl/hydrogen rate ratios mentioned before thus indicate conclusively that the solvolyses of simple cyclopropyl derivatives are k_Δ processes. Ring opening is concerted with ionization and the anchimeric assistance is provided by the electrons of the C_2–C_3 bond moving toward the backside of the C_1–X bond in the favored mode of disrotatory ring opening (Figure 2). Conceptually the solvolysis of a cyclopropyl derivative can be regarded as an "internal SN2" reaction with the electrons from the breaking C_2–C_3 bond taking the place of the attacking nucleophile.[11b]

The amount of anchimeric and torsional strain assistance in cyclopropyl tosylate was estimated as a factor of 10^7 in rate by Foote,[9a] based on the carbonyl

(33) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 5386 (1969).

(34) This dependence of the OTs/Br rate ratio on solvent, lower values being observed in aqueous solvents, is commonly found.[35]

(35) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2538 (1970), and references therein; (b) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

(36) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 93, 3189 (1971).

(37) (a) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); (b) see ref 24a, pp 63–65.

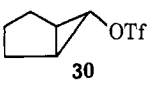
(38) A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, 90, 1904 (1968), and papers therein cited.

(39) For definitions and a discussion of k_s, k_Δ, and k_c see: P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, 92, 2542 (1970).

(40) (a) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948), and subsequent papers in this series; (b) ref 24a, pp 45–49, 171.

(41) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 5977 (1970), and references therein.

stretching frequency of cyclopropanone. On the same basis, but applying a correction for torsional strain, Schleyer[9b] estimated the anchimeric assistance as a factor of 10^2. A more accurate estimate of the amount of anchimeric assistance in the cyclopropyl system can be made, based on the reactivity of cyclopropyl triflate (**15**) relative to that of *exo*-bicyclo[3.1.0]hex-6-yl triflate (**30**). This latter compound (**30**) is geometrically biased against undergoing the favored mode of disrotatory ring opening, a trans double bond in a six-membered ring would result, and **30** solvolyzes 26,500 times slower



30

than **15** in acetic acid at 25° to give about 50% product of retained configuration.[1e,33] Since the rate of **30** may be itself somewhat accelerated and since the trimethylene group attached to the β positions in **30** should be at least somewhat inductively rate enhancing, the observed factor of $10^{4.4}$ ($10^{4.1}$ in 50% EtOH, 25°) for k_{15}/k_{30} is a minimum value for the anchimeric assistance present in the parent cyclopropyl system. A second, independent estimate of this anchimeric assistance can be made, based on the α-methyl/hydrogen rate ratio for cyclopropyl tosylate (k_{24}/k_1 = 1080, 25°, HOAc). Using the provisional limiting value of 10^8 from the 2-adamantyl system for the "normal" α-methyl/hydrogen rate ratio,[24b] the anchimeric assistance in cyclopropyl tosylate (**1**) is estimated to be at least a factor of 10^5. Again, this is a minimum value estimate, because the rate of 1-methylcyclopropyl tosylate (**24**) should be itself accelerated by anchimeric assistance.

Conclusions

The various β-methyl-substituted cyclopropyl tosylates undergo concerted stereospecific ring opening by the favored disrotatory mode on acetolysis. This is demonstrated by a correlation of the observed rates with a treatment based on electronic and steric effects in ground and transition states, assuming the protoallylic transition state in each case expected from the favored mode of disrotatory ring opening. Standard mechanistic criteria [m, $(k_{\text{aq alc}}/k_{\text{AcOH}})_Y$, α-CH_3/H, and OTs/Br rate ratios] show unambiguously the k_Δ nature of parent cyclopropyl solvolyses, and the amount of anchimeric assistance in this system is at least a factor of 10^4–10^5 in rate at 25°.

Experimental Section

Melting points were determined with a Mettler FP-15 melting point apparatus connected to a strip chart recorder. All melting and boiling points are uncorrected. Nmr spectra were taken on a Varian Model A60-A spectrometer using tetramethylsilane as internal standard. Infrared spectra were taken on a Perkin-Elmer Model 237B grating spectrometer. Preparative gas chromatography was performed on a Varian Aerograph Model 1520 gas chromatograph. Microanalyses were performed at FMC Corp., Princeton, N. J., or Galbraith Laboratories, Knoxville, Tenn.

Cyclopropanol (11). Cyclopropanol was prepared by the modified Cottle procedure.[11] A solution of $MgBr_2$ was prepared (under N_2) from 8.2 g of Mg and 54 g of Br_2 in *ca.* 250 ml of dry ether. To this solution, in a three-necked 2-l. flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, and N_2 inlet, 31 g of epichlorohydrin in 50 ml of ether was added dropwise over a 30-min period. During addition the solution turned dark red and an orange solid appeared. The solution was stirred for 1 hr, and 0.5 g of $FeCl_3 \cdot 6H_2O$ was added as a catalyst. A freshly prepared solution of EtMgBr (from 66 g of ethyl bromide and 15 g of Mg in 800 ml of ether) was added dropwise over a 4-hr period and the reaction mixture was then allowed to stir for 10 hr. The reaction was then cooled in ice and hydrolyzed with 500 ml of iced ammonium chloride solution. The mixture was filtered and the layers separated. The ether layer was extracted with 8 × 100 ml of water, and then *only these aqueous extracts* were continuously extracted with ether for 3 days. The ether was stripped and the residue distilled. The fractions boiling between 50 and 70° (100 mm) were about 60% cyclopropanol. The pure cyclopropanol (*ca.* 5 g) was isolated by preparative glpc using a 20-ft × 0.25-in. column, 10% Carbowax 20M on 30–60 Chromosorb W: nmr (neat) τ 4.50 (s, 1, CHO*H*), 5.54 (m, 1, C*H*OH), 9.35–9.58 (m, 4).

Cyclopropyl Tosylate (1). Cyclopropanol (1.8 g, 0.31 mol) and freshly recrystallized tosyl chloride (9.6 g, 0.05 mol) gave by the normal pyridine procedure[42] 2.2 g (33%) of the clear liquid tosylate **12** which crystallized on long standing at −10°: nmr (CCl_4) τ 2.49 (AB q, 4, aromatic), 6.12 (m, 1, C*H*OTs), 7.58 (s, 3, C*H*$_3$), 9.30–9.55 (m, 4).

Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.17; H, 5.51.

Cyclopropyl *p*-Nitrobenzenesulfonate (13). The normal pyridine method was used with 0.9 g (0.015 mol) of cyclopropanol and 5.4 g (0.023 mol) of freshly recrystallized *p*-nitrobenzenesulfonyl chloride giving 1.4 g (42%) of solid **13**. Recrystallization from 30–60° petroleum ether at −78° gave a light brown solid: mp 164° (dec); nmr (CCl_4) τ 1.6 (AB q, 4, aromatic), 5.87 (m, 1, C*H*ONs), 9.15–9.38 (m, 4).

Anal. Calcd for $C_9H_9NO_5S$: C, 44.44; H, 3.73; N, 5.76. Found: C, 44.71; H, 3.27; N, 5.82.

Cyclopropyl 2,4-Dinitrobenzenesulfonate (14). The method of Lunt[43] was employed. A solution of 0.75 g (0.0125 mol) of cyclopropanol in 25 ml of 2,6-lutidine was cooled to 0° and 3.5 g (0.0125 mol) of 2,4-dinitrobenzenesulfonyl chloride was added with stirring over a 20-min period. After stirring this for 0.5 hr more, 20 ml of toluene was added and stirring was continued at 0° for 1 hr. The slurry was then poured into 50 ml of ice water. Two layers formed, with a gelatinous solid above the water layer. This solid containing toluene layer was separated, washed with water, and dried over $MgSO_4$. After filtration, about 7 vol of 60–70° petroleum ether were added. The resulting cloudy solution was allowed to stand overnight at 0°, after which the fluffy tan precipitate **14** (0.58 g, 15%) was filtered, dried *in vacuo*, and stored in the cold. Two further recrystallizations gave a very light fluffy solid: mp 95–96° (dec); nmr ($CDCl_3$) τ 1.14–1.62 (m, 3, aromatic), 5.70 (m, 1, C*H*OR), 8.95–9.30 (m, 4).

Anal. Calcd for $C_9H_8N_2O_7S$: C, 37.50; H, 2.80; N, 9.72. Found: C, 37.07; H, 2.94; N, 9.30.

Cyclopropyl Trifluoromethanesulfonate (15). A solution of 1.0 g (0.017 mol) of cyclopropanol in 30 ml of dry pyridine was cooled to 0° and 5.0 g (0.017 mol) of trifluoromethanesulfonic anhydride[44] was added slowly with stirring. The mixture was allowed to stand for 2 hr at 5° and then worked up in the manner normal for a liquid tosylate.[42] On attempting to evaporate the ether, however, difficulty was encountered. Due to the high volatility of the product, most of the ester was lost. The little that remained was dissolved in a minimal amount of 30–60° petroleum ether and forced out of solution by cooling to −78°. Here again, it was not possible to dry the product *in vacuo*. The ether was merely decanted at −78° under N_2 and the liquid product stored at 5°. (When exposed to air the triflate completely evaporated after 25 min.) Some petroleum ether (*ca.* 25%) remained in the *ca.* 150 mg of liquid product. Kinetics on this triflate were perforce done conductometrically. The ir [(CCl_4) 1424, 1250, 1215, 1150, 1035, 952, and 870 cm^{-1}] and nmr [(CCl_4) τ 5.47 (m, C*H*OTf), 8.8–9.2 (m, ring protons)] spectra indicate conclusively the desired product.

Alkyl-Substituted Cyclopropyl Tosylates. The substituted cyclopropyl tosylates (**21–23**, **27**, and **28**) were prepared as described previously.[19] It was found that commercial methyllithium in ether

(42) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1180.

(43) E. Lunt, May and Baker Laboratory Bulletin, 1958, Vol. 3, p 13; see D. Chadbourne and A. Nunn, *J. Chem. Soc.*, 4458 (1965).

(44) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *ibid.*, 2574 (1957); we are grateful to Dr. R. L. Hansen, Minnesota Mining and Manufacturing Co., for a generous gift of trifluoromethanesulfonic acid.[45]

(45) For information about this acid and its derivatives see Minnesota Mining and Manufacturing Co., Technical Information, "FC-24—Trifluoromethanesulfonic Acid."

(made from CH_3Cl) would not suffice for the carbene generation reactions in these syntheses as it contained no LiI. Moreover, freshly prepared methyllithium (made from CH_3I) could not be used either, but had to be set aside for several days to allow the finely suspended salts to settle out of the ether solution. The clear solution could then be decanted from the settled salts and used by itself or with 1–2 parts of commercial methyllithium in the carbene reactions.

2-Chloroethyl *trans*-2-Methylcyclopropyl Ether (19a) and 2-Chloroethyl *cis*-2-Methylcyclopropyl Ether (19b). Dichloromethyl 2-chloroethyl ether (**17**)[46] (58.0 g, 0.35 mol) in 750 ml of dry ether was cooled to −78° in a 3-l. three-necked flask fitted with a dropping funnel, thermometer, magnetic stirrer, N_2 inlet, and Dry Ice condenser. About 150 g of propylene (Matheson, C.P. Grade) was bubbled slowly into the solution. It was then necessary to raise the solution temperature to −10 to 0°, since this is the lowest temperature at which carbene generation occurs. To accomplish this it was necessary to distil the propylene (bp −40°) into another flask, so an adapter (functioning as an inverted Y tube) and a second receiver flask were added to the system; this permitted the Dry Ice condenser to condense the propylene into whichever flask was desired, by simply reversing the Y adapter. When the propylene was distilled into the second receiver the reaction vessel was heated to 0° with a water bath. Then the Y adapter was reversed, and the propylene distilled back into the reaction vessel. At the same time, methyllithium in diethyl ether (*vide supra*) was added dropwise. External heating, methyllithium addition, and introduction of propylene were continued until the refluxing of the propylene drove the reaction temperature below −10°. At this point addition of methyllithium was stopped, the propylene distilled into the second receiver, and the reaction temperature raised to 0–5°. This sequence repeated until a positive Gilman test[47] for excess methyllithium was obtained. The unreacted propylene was then allowed to distil away and the reaction mixture was hydrolyzed by adding 200 ml of water, slowly at first. The ethereal layer was separated and the water layer extracted with three 100-ml portions of ether. The combined ether solutions were dried over Na_2SO_4, the solvent was evaporated, and the residue was distilled to give 16.2 g (34%) of **19**, bp 83–87° (81 mm). The nmr indicated a cis/trans ratio of about 4/1. The individual ether isomers **19a** [nmr (CCl_4) τ 6.1–6.6 (m, $ClCH_2CH_2$–, 4), 7.04 (m, >C*H*OR, 1), 8.85 (s, –CH_3, 3), 8.7–10.0 (m, 3)] and **19b** [nmr (CCl_4) τ 6.1–6.6 (m, $ClCH_2CH_2$–, 4), 6.76 (d of t, J_d = 6 Hz, J_t = 10 Hz, >C*H*OR, 1), 8.92 (s, CH_3, 3), 8.7–10.0 (m, 3)] could be separated with difficulty by preparative glc using a double column (50-ft × $^3/_8$-in. 30% FFAP on 30–60 Chrom W coupled to 20-ft × $^3/_8$-in. 20% SE-30 on 30–60 Chrom W).

***trans*-2-Methylcyclopropanol (20a) and *cis*-2-Methylcyclopropanol (20b).** A solution of 10.0 g (0.017 mol) of the mixture of isomers **19** and 25 ml of dry ether was placed in a 500-ml three-necked flask fitted with dropping funnel, reflux condenser, magnetic stirrer, and a N_2 inlet. *n*-Butyllithium in hexane (Foote) was added dropwise, maintaining gentle reflux, until a positive Gilman test[47] was obtained. The milky solution was stirred for 2 hr and then hydrolyzed with 100 ml of saturated $NaHCO_3$ solution. The layers were separated and the water layer was extracted with 50 ml of ether. The combined organic solutions were dried over Na_2SO_4, the solvent was evaporated, and the residue was distilled to give 1.0 g (19%) of **20**: bp 60–62° (40 mm); nmr (CCl_4) τ 5.07 (s, >CHO*H*, 1), 6.71 [d of t, J_d = 7 Hz, J_t = 11 Hz, C*H*OH (**20b**), 0.8], 7.03 [m, C*H*OH (**20a**), 0.2], 8.96 [m, CH_3 (**20b**), 2.4], 9.13 [d, J = 6 Hz, CH_3 (**20a**), 0.6]. The individual isomers were prepared later by the same procedure: 1.25 g of **19a** gave 0.63 g (94%) of **20a**, bp 60° (40 mm), and 4.1 g of **19b** gave 1.8 g (82%) of **20b**, bp 63–64° (42 mm).

***trans*-2-Methylcyclopropyl Tosylate (12a) and *cis*-2-Methylcyclopropyl Tosylate (12b).** The epimeric alcohol mixture (**20**, **20b**/**20a** ~4/1) was used in the usual pyridine tosylation procedure;[42] 0.42 g (0.058 mol) of **20** and 1.25 g (0.066 mol) of tosyl chloride gave 0.59 g (48%) of the liquid tosylate mixture **12**; nmr showed the trans:cis isomer ratio to be about 1:4.

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.16; H, 6.73.

After difficulty was encountered separating the rates of **12a** and **12b** kinetically (the trans isomer gives a dark-colored solution which renders the end point of the cis material difficult to determine), the individual isomers of **20** were used to prepare the pure tosylates **12a** [nmr (CCl_4) τ 2.41 (ABq, –C_6H_4–, 4), 5.41 (m, >C*H*OTs, 1), 7.53 (s, $C_6H_4CH_3$, 3), 9.06 (s, >CHCH_3, 3), 8.75–9.80 (m, 3)] and **12b** [nmr (CCl_4) τ 2.42 (ABq, –C_6H_4–, 4), 6.07 (m, >C*H*OTs, 1), 7.55 (s, –$C_6H_4CH_3$, 3), 8.96 (s, >CHCH_3, 3), 8.85–9.75 (m, 3)].

***cis*-2,3-Dimethylcyclopropyl Tosylate (21b).** A solution of 5.1 g (0.021 mol) of the isomeric mixture **21**[19] (**21b**/**21a** ~ 4/1 by nmr) in 50 ml of anhydrous acetic acid buffered with 2 equiv of NaOAc was heated at 100° for 2 hr. The solution was then neutralized with solid $NaHCO_3$ and extracted with 3 × 25 ml of pentane. The pentane extracts were dried over Na_2SO_4 and evaporated. The oily residue was dissolved in a minimum amount of 30–60° petroleum ether, treated with activated charcoal (Darco), and filtered. The filtrate was cooled to −78°, the liquid was decanted, and the product remaining was dried *in vacuo*. This purification treatment was repeated (no Darco) to give 2.5 g (~66%) of pure liquid **21b**: nmr (CCl_4) τ 2.45 (AB q, –C_6H_4–, 4), 6.07 (m, >C*H*OTs, 1), 7.58 (s, –$C_6H_4CH_3$, 3), 9.18 (m, 8).

Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 60.04; H, 6.60.

***cis*-2,2,3-Trimethylcyclopropyl Tosylate (22b).** Analogous to the procedure for obtaining **21b**, the pure isomer **22b** was prepared by preparative solvolysis of **22**:[19] 6.0 g (0.024 mol, **22b**/**22a** ~ 5/7 by nmr) of **22** was heated in buffered acetic acid at 100° for 75 min and, after purification, 1.3 g (~50%) of liquid **22b** [nmr (CCl_4) τ 2.54 (AB q, C_6H_4, 4), 6.41 (d, J = 6.5 Hz, C*H*OTs, 1), 7.60 (s, –$C_6H_4CH_3$, 3), 8.95–9.4 (m, 10)] was recovered.

Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.05, H, 7.00.

1-Methylcyclopropyl Tosylate (24). 1-Methylcyclopropanol, prepared by the method of DePuy, *et al.*,[48] was converted by the standard pyridine procedure[42] to the liquid tosylate (**24**) which crystallized on long standing in the cold: mp *ca.* 10°; nmr (CCl_4) τ 2.50 (AB q, 4, –C_6H_4–), 7.55 (s, 3, –$C_6H_4CH_3$), 8.42 [s, 3, C(CH_3)OTs], 8.91 (m, 2), 9.45 (m, 2). While a satisfactory analysis for **24** was not obtained, acetolyses proceeded with good first-order kinetics and gave experimental infinities corresponding to *ca.* 100% reaction.

Kinetic Procedures. Anhydrous acetic acid was prepared by distillation from acetic anhydride. Absolute ethanol was purified by the method of Lund and Bjerrum.[49] Aqueous ethanol solvents were prepared by mixing this solvolytic ethanol (v/v) with the appropriate amounts of freshly boiled distilled water. Substrate concentrations for titrimetric kinetics were 0.025–0.03 *M*. The method of Winstein[21] was employed for titrimetric tosylate acetolyses. Where the amount of material on hand was limited, satisfactory results were obtained with 1-ml aliquots instead of the 5-ml portions usually employed. When titrating the liberated toluenesulfonic acid with NaOAc in HOAc in the tosylate acetolyses, a light underneath the titration flask was found to facilitate observation of the crystal violet end point. Acetolyses of cyclopropyl bromide (**16**) were carried out in anhydrous acetic acid buffered with 0.032 *M* NaOAc, and all solvolyses were followed by Volhard titrations for liberated bromide.[22] In aqueous tosylate solvolyses, where the liberated acid was titrated with standard base, addition of a few milliliters of water to each titration flask was found to sharpen the brom thymol blue end point. Experimental infinities for titrimetric kinetics were usually within 5% of the theoretical values. Kinetics for cyclopropyl triflate (**15**) were followed conductometrically using special glass cells with bright platinum electrodes and a recording Wheatstone bridge.[50] Substrate concentration for conductometric kinetic was ~10^{-3} *M*. Infinity conductances for **15**, checked against known concentrations of trifluoromethanesulfonic acid, corresponded to 70–75% reaction. All solvolyses displayed good first-order kinetics and were followed to 90% reaction. Nine titrimetric points or 10–15 conductometric points were usually taken per kinetic run. First-order rate constants were determined using a modified version of the LSKIN computer program.[51]

Acknowledgments. We wish to thank the National Science Foundation, the donors of the Petroleum

(46) H. Gross, A. Rieche, and E. Höft, *Chem. Ber.*, 94, 544 (1961).
(47) H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, 47, 2002 (1925).
(48) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, 29, 2813 (1964).
(49) H. Lund and J. Bjerrum, *Chem. Ber.*, 64, 210 (1931); see L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 285.
(50) For details of cell and bridge construction see: C. J. Lancelot, Ph.D. Thesis, Princeton University, 1971.
(51) D. F. Detar in "Computer Programs for Chemistry," Vol. I, D. F. Detar, Ed., Benjamin, New York, N. Y., 1968, pp 126–173.

Research Fund, administered by the American Chemical Society, and Hoffmann–LaRoche, Nutley, N. J., for support of this research at Princeton University, and the Deutschen Forschung-Gemeinschaft and the Fonds der Chemischen Industrie for support of the work at the University of Göttingen. We are grateful to Mr. P. R. Isele for preparation and solvolysis of 1-methylcyclopropyl tosylate.

Cyclopropyl Solvolyses. IV. Leaving Group and Alkyl Substitution Effects in Monocyclic Systems[1]

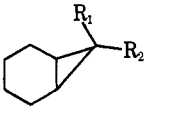
W. F. Sliwinski,[2a] T. M. Su,[2b] and P. v. R. Schleyer*

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08540. *Received April 22, 1971*

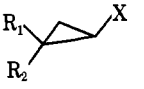
Abstract: The acetolysis rates of a number of alkyl- and polymethyl-substituted cyclopropyl tosylates, bromides, and chlorides have been determined. The kinetic results in all cases are consistent with stereospecific disrotatory ring opening concerted with ionization. For *trans*-β-alkyl substitution the observed rates show a regular but rather modest increase in the order $CH_3 < C_2H_5 < i\text{-}C_3H_7 < tert\text{-}C_4H_9$, attributed to inductive effects. The corresponding cis isomers show little variation; we attribute this to a combination of opposing steric and inductive effects. A comparison of α-phenyl and α-methyl substituent effects with those found in other secondary systems provides an estimate of the anchimeric assistance in cyclopropyl tosylate solvolysis in the range $10^{4.6}$–10^{7}. We conclude that methyl rather than phenyl groups are preferable as probes for detecting nonclassical charge delocalization at positions remote from the site of attachment of the leaving group. The degree of ring opening at the transition state for a given cyclopropyl system does not appear to change significantly with a change in leaving group. The rate enhancements provided by trans-β substituents follows the leaving group order Cl > Br > OTs; we attribute this to electronic effects. Ground-state steric effects are a significant factor in the reactivity of cis-β substituted cyclopropyl systems. The order of leaving group steric size in these cyclopropyl systems is Br > Cl > OTs, which parallels the van der Waals' radii of the atoms involved (Br > Cl > O).

The solvolyses of cyclopropyl derivatives tend strongly to proceed with concerted disrotatory ring opening.[1,3–5] At least partial ring opening is simultaneous with departure of the leaving group in almost all cases leading to a transition state in which the positive charge is delocalized over all three-ring carbon atoms; eventually ring-opened allyl products are produced.[6] The effect of a change in the leaving group on the reactivity of cyclopropyl derivatives has, however, received little attention.

1



2a (*exo*), $R_1 = H$; $R_2 = X$
2b (*endo*), $R_1 = X$; $R_2 = H$



3a (*trans*), $R_1 = H$; $R_2 = C_6H_5$
3b (*cis*), $R_1 = C_6H_5$; $R_2 = H$

An apparent discrepancy in the solvolysis results for the bicyclo[4.1.0]hept-7-yl (7-norcaryl) system, **2**, led to the present investigation. Cristol, Sequeira, and DePuy had reported that while the *endo*-chloride **2b** (X = Cl) was readily acetolyzed at 124.6° ($k = 1.4 \times 10^{-6}$ sec^{-1}), the *exo*-chloride was inert under these conditions;[9] they concluded that the endo/exo reactivity ratio was at least a factor of 200 and possibly much more. In contrast we found the endo/exo rate ratio for **2** (X = OTs) to be only 36 in acetic acid at 100°.[5a] Such differences in relative reactivity for a mere change of leaving group are quite unexpected. In addition, a smaller but *reversed* leaving group dependence has been found in the 2-phenylcyclopropyl system, **3**, where the trans/cis rate ratio for acetolysis at 100° is 20 for X = OTs and 4 for X = Br or Cl.[10]

(1) Part III: preceding paper, P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, 94, 125 (1972).

(2) (a) Ph.D. Thesis, Princeton University, 1971; National Science Foundation Predoctoral Fellow, 1965–1967; American Machine and Foundry Fellow, 1967–1969; (b) Ph.D. Thesis, Princeton University, 1970; Petroleum Research Fund Predoctoral Fellow, 1968–1969.

(3) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965); (b) see also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

(4) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, 87, 4006 (1965).

(5) (a) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967); (b) D. B. Ledlie and E. A. Nelson, *ibid.*, 1175 (1969); (c) D. T. Clark and G. Smale, *Chem. Commun.*, 868 (1969).

(6) Exceptional cases giving at least some cyclopropyl products[5] include several amine deaminations,[7] and the solvolyses of 1-bicyclopropyl derivatives **1**[8a–c] and the remarkable 1-thiophenoxycyclopropyl chlorides.[8d]

(7) (a) P. Lipp and C. Padberg, *Ber. Deut. Chem. Ges. B*, 54, 1316 (1921); R. Pettit, *J. Amer. Chem. Soc.*, 82, 1972 (1960); (c) H. Hart and R. H. Martin, *ibid.*, 82, 6362 (1960); (d) W. Kirmse and H. Schütte, *ibid.*, 89, 1284 (1967); (e) W. Kirmse and H. Schütte, *Chem. Ber.*, 101, 1674 (1968); (f) W. Kirmse and F. Scheidt, *ibid.*, 103, 3711 (1970).

(8) (a) J. A. Landgrebe and L. W. Becker, *J. Amer. Chem. Soc.*, 89, 2502 (1967); (b) J. A. Landgrebe and L. W. Becker, *ibid.*, 90, 395 (1968); (c) B. A. Howell and J. G. Jewett, *ibid.*, 93, 798 (1971); (d) U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, *Tetrahedron Lett.*, 5077 (1970).

(9) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Amer. Chem. Soc.*, 87, 4007 (1965).

(10) (a) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, 88, 3343 (1966); (b) J. W. Hausser and N. J. Pinkowski, *ibid.*, 89, 6981