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]

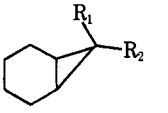
W. F. Sliwinski,[2a] T. M. Su,[2b] and P. v. R. Schleyer*

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

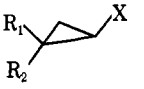
Abstract: The acetolysis rates of a number of alkyl- and polymethyl-substituted cyclopropyl tosylates, bromides, and chlorides have been determined. The kinetic results in all cases are consistent with stereospecific disrotatory ring opening concerted with ionization. For *trans*-β-alkyl substitution 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

Table I. Rates of Acetolysis of 2-Alkylcyclopropyl Derivatives[a]

Compd	Leaving group	Substituent	Temp, °C	k_1,[b] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
4a	OTs	*trans*-CH_2CH_3	125.0	$(1.00 \pm 0.03) \times 10^{-5}$	29.8	−2.7
			150.0	$(9.80 \pm 0.15) \times 10^{-4}$		
			100.0	7.55×10^{-6}		
			25.0	2.50×10^{-10}		
4b	OTs	*cis*-CH_2CH_3	150.0	$(4.76 \pm 0.03) \times 10^{-5}$	30.9	−6.1
			175.0	$(3.91 \pm 0.04) \times 10^{-4}$		
			100.0	3.06×10^{-7}		
			25.0	6.91×10^{-12}		
5a	OTs	*trans*-$CH(CH_3)_2$	123.9	$(1.15 \pm 0.04) \times 10^{-4}$	29.8	−2.0
			150.0	$(1.267 \pm 0.002) \times 10^{-3}$		
			100.0	9.63×10^{-6}		
			25.0	3.09×10^{-10}		
5b	OTs	*cis*-$CH(CH_3)_2$	150.0	$(5.975 \pm 0.004) \times 10^{-5}$	31.8	−3.3
			185.0	$(1.167 \pm 0.006) \times 10^{-3}$		
			100.0	3.30×10^{-7}		
			25.0	5.37×10^{-12}		
6a	OTs	*trans*-$C(CH_3)_3$	100.0	$(1.38 \pm 0.03) \times 10^{-5}$	29.0	−3.6
			125.0	$(1.71 \pm 0.03) \times 10^{-4}$		
			25.0	5.97×10^{-10}		
6b	OTs	*cis*-$C(CH_3)_3$	150.0	$(4.14 \pm 0.10) \times 10^{-5}$	32.3	−2.9
			175.0	$(3.75 \pm 0.12) \times 10^{-4}$		
			100.0	2.11×10^{-7}		
			25.0	2.90×10^{-12}		
7a	Br	*trans*-CH_3	124.8	$(1.411 \pm 0.001) \times 10^{-5}$	30.9	−3.6
			149.9	$(1.53 \pm 0.02) \times 10^{-4}$		
			100.0	9.87×10^{-7}		
			25.0	2.17×10^{-11}		
7b	Br	*cis*-CH_3	150.0	$(1.20 \pm 0.02) \times 10^{-5}$	31.4	−7.7
			175.0	$(1.02 \pm 0.03) \times 10^{-4}$		
			100.0	7.17×10^{-8}		
			25.0	1.38×10^{-12}		
8a	Br	*trans*-$C(CH_3)_3$	125.0	$(2.30 \pm 0.01) \times 10^{-5}$	30.6	−3.5
			150.0	$(2.40 \pm 0.06) \times 10^{-4}$		
			100.0	1.62×10^{-6}		
			25.0	4.02×10^{-11}		
8b	Br	*cis*-$C(CH_3)_3$	150.0	$(2.53 \pm 0.01) \times 10^{-5}$	31.7	−5.3
			175.0	$(2.20 \pm 0.02) \times 10^{-4}$		
			100.0	1.42×10^{-7}		
			25.0	2.39×10^{-12}		
9a	Cl	*trans*-$C(CH_3)_3$	175.0	$(1.28 \pm 0.08) \times 10^{-4}$	30.7	−8.7
			201.85	$(9.51 \pm 0.35) \times 10^{-4}$		
			100.0	1.05×10^{-7}		
			25.0	2.53×10^{-12}		
9b	Cl	*cis*-$C(CH_3)_3$	175.0	$(7.57 \pm 0.22) \times 10^{-6}$	32.6	−10.1
			202.65	$(6.73 \pm 0.22) \times 10^{-5}$		
			100.0	4.04×10^{-9}		
			25.0	5.14×10^{-14}		

[a] Anhydrous acetic acid, ~0.03 *M* in substrate; 0.032 *M* NaOAc added as buffer for halide acetolyses. [b] Average deviation of two or more kinetic determinations. Rate constants at 25.0 and 100.0° are calculated values.

We report here an extensive study of leaving group effects in cyclopropyl systems. In addition, steric and electronic effects of alkyl substitution on cyclopropyl solvolysis are analyzed.[1,11]

Procedures and Results

Alkyl-substituted cyclopropyl tosylates were synthesized by the method of Schöllkopf.[1,12] Bromocyclopropanes were obtained by tri-*n*-butyltin hydride reduction of the corresponding *gem*-dibromocyclopropanes,[13] prepared by dibromocarbene addition to the desired olefins.[14] Chlorocyclopropanes were prepared directly by the chlorocarbene addition procedure of Closs and Closs.[15] Where mixtures of isomers were obtained, the individual isomers were usually separated by spinning-band distillation or preparative glc. Stereochemical assignments of cyclopropyl derivatives are based on the vicinal coupling constants of the distinctive α protons in the nmr spectra ($J_{HH\,cis} > J_{HHtrans}$).[1]

Acetolysis rates of all compounds were determined titrimetrically as described previously.[1] All halide acetolyses were carried out in acetic acid buffered with an excess of sodium acetate, and were followed by Volhard titrations[16] for liberated halide. Good first-order behavior was observed to greater than 90% reaction in all cases.

(1967); (c) J. W. Hausser and M. J. Grubber, private communication; *cf.* M. J. Grubber, Ph.D. Thesis, Duquesne University, 1968; the original authors suggested that concerted ring opening in the *cis*-2-phenylcyclopropyl halides might be occurring by the "wrong" or disfavored disrotatory mode, but results in other systems render this unlikely.

(11) *Cf.* P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966).

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

(13) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(14) (a) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409, 5430 (1956).

(15) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

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

Table II. Rates of Acetolysis for Cyclopropyl Halides[a]

Compd	Leaving group	Substituents	Temp, °C	k_1,[b] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
10a	Br	*trans,trans*-2,3-Dimethyl	78.0	$(7.39 \pm 0.03) \times 10^{-5}$	27.1	−0.7
			100.6	$(8.20 \pm 0.08) \times 10^{-4}$		
			100.0	7.72×10^{-4}		
			25.0	6.32×10^{-8}		
10b	Br	*cis,cis*-2,3-Dimethyl	150.6	$(3.092 \pm 0.008) \times 10^{-5}$	33.3	−1.3
			174.9	$(2.79 \pm 0.001) \times 10^{-4}$		
			100.0	1.28×10^{-7}		
			25.0	1.26×10^{-12}		
11a	Cl	*trans,trans*-2,3-Dimethyl	100.35	$(2.53 \pm 0.02) \times 10^{-5}$	29.1	−2.2
			124.3	$(2.85 \pm 0.03) \times 10^{-4}$		
			100.0	2.43×10^{-5}		
			25.0	1.01×10^{-9}		
11b	Cl	*cis,cis*-2,3-Dimethyl	175.0	$(8.79 \pm 0.11) \times 10^{-6}$	34.6	−5.2
			201.05	$(7.88 \pm 0.03) \times 10^{-5}$		
			100.0	2.96×10^{-9}		
			25.0	1.88×10^{-14}		
12	Br	*cis,trans*-2,3-Dimethyl	100.5	$(1.59 \pm 0.03) \times 10^{-5}$	28.5	−4.6
			124.7	$(1.76 \pm 0.01) \times 10^{-4}$		
			100.0	1.51×10^{-5}		
			25.0	7.52×10^{-10}		
13	Cl	*cis,trans*-2,3-Dimethyl	150.3	$(5.61 \pm 0.02) \times 10^{-5}$	31.5	−4.3
			170.3	$(3.18 \pm 0.03) \times 10^{-4}$		
			100.0	3.18×10^{-7}		
			25.0	5.79×10^{-12}		
14a	Br	*trans*-2,2,3-Trimethyl	50.5	$(2.38 \pm 0.03) \times 10^{-5}$	23.8	−6.3
			75.1	$(3.50 \pm 0.11) \times 10^{-4}$		
			100.0	3.72×10^{-3}		
			25.0	9.23×10^{-7}		
14b	Br	*cis*-2,2,3-Trimethyl	124.7	$(1.17 \pm 0.04) \times 10^{-4}$	28.0	−6.8
			149.9	$(1.02 \pm 0.06) \times 10^{-3}$		
			100.0	1.05×10^{-5}		
			25.0	6.40×10^{-10}		
15a	Cl	*trans*-2,2,3-Trimethyl	100.4	$(8.28 \pm 0.16) \times 10^{-5}$	28.2	−2.2
			124.7	$(8.98 \pm 0.21) \times 10^{-4}$		
			100.0	7.98×10^{-5}		
			25.0	4.50×10^{-9}		
15b	Cl	*cis*-2,2,3-Trimethyl	159.9	$(6.78 \pm 0.04) \times 10^{-5}$	33.3	−1.5
			179.9	$(3.91 \pm 0.08) \times 10^{-4}$		
			100.0	1.18×10^{-7}		
			25.0	1.18×10^{-12}		
16	Br	2,2,3,3-Tetramethyl	75.1	$(1.25 \pm 0.05) \times 10^{-4}$	28.3	4.5
			100.1	$(2.06 \pm 0.04) \times 10^{-3}$		
			100.0	2.04×10^{-3}		
			25.0	1.11×10^{-7}		

[a] Anhydrous acetic acid buffered with 0.032 *M* NaOAc; ~0.025–0.03 *M* in substrate. [b] Average deviation of two or more kinetic determinations. Rate constants at 25.0 and 100.0° are calculated values.

Table III. Relative Rates of 2-Substituted Cyclopropyl Derivatives

Compd	Leaving group	2 substituent	$k_{rel,100°}$[a] Trans	$k_{rel,100°}$[a] Cis	k_{trans}/k_{cis}	Ref
17	OTs[b]	$-CH_3$	138	5.7	24	*e*
4		$-CH_2CH_3$	180	7.4	24	*c*
5		$-CH(CH_3)_2$	230	8	29	*c*
6		$-C(CH_3)_3$	330	5	66	*c*
7	Br[b]	$-CH_3$	630	46	14	*c*
8		$-C(CH_3)_3$	1040	92	11	*c*
18	Br[d]	$-CH_2CH_3$	460	20	23	*f*
19		$-CH{=}CH_2$	1770	160	11	*f*
20		*c*-C_3H_6	7350	290	25	*f*

[a] All rates are relative to those of the parent cyclopropyl derivatives: cyclopropyl tosylate (**21**), k(100°, HOAc) = 4.16×10^{-8} sec^{-1}; cyclopropyl bromide (**22**), k(100°, HOAc) = 1.55×10^{-9} sec^{-1}, k(100°, 50% EtOH) = 2.18×10^{-7} sec^{-1}. [b] In acetic acid. [c] This work. [d] In 50% EtOH. [e] Reference 1. [f] J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, **33**, 1173 (1968).

First-order rate constants and thermodynamic activation parameters were determined by least-squares computer programs and are summarized in Tables I and II. Tables III and IV give the relative rates and isomeric rate ratios for the various mono-β-substituted cyclopropyl derivatives, including the available data from the literature. Relative rates for the various β-methyl-substituted cyclopropyl derivatives are presented in Table V.

Discussion

Electronic Substituent Effects. The kinetic results in all cases are consistent with concerted, stereospecific

Table IV. β-Substitution Effects for Various Leaving Groups. Relative Acetolysis Rates at 100°

Compd	2 substituent	Leaving group	k_{rel}[a] Trans	Cis	k_{trans}/k_{cis}	Ref
6	$-C(CH_3)_3$	OTs	330	5	66	*b*
8		Br	1040	92	11	*b*
9		Cl	5830	220	26	*b*
3 (X = OTs)	$-C_6H_5$	OTs	300	15	20	*c*
3 (X = Br)		Br	5310	1330	4	*d*
3 (X = Cl)		Cl	9340	2300	4	*e*

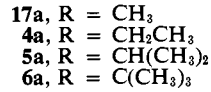
[a] Rates are relative to the parent cyclopropyl derivatives. The rate constant of cyclopropyl chloride (**23**) in acetic acid at 100° is estimated as 1.8×10^{-11} sec^{-1} from the data of Roberts and Chambers (J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951)) assuming the same solvent and temperature dependence for **23** as was found for cyclopropyl bromide (**22**).[1] (This estimate of the reactivity of cyclopropyl chloride is slightly higher (by a factor of 1.5–5) than previous estimates[10b] (J. A. Landgrebe and D. E. Applequist, *J. Amer. Chem. Soc.*, **86**, 1536 (1964)) and is also higher than the value which would be obtained using Brown's factor (H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964)) of 8.5×10^{-5} for k_{Cl}/k_{OTs} in secondary systems. A slightly lower estimated rate for **23** would in no way affect our conclusions.) See also Table III, footnote *a*. [b] This work. [c] Reference 10a. [d] Reference 10c. [e] Reference 10b.

Table V. Relative Acetolysis Rates of β-Methyl-Substituted Cyclopropyl Derivatives

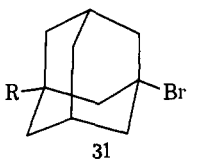
Substituents	Relative rates at 100°[a,b] OTs[c]	Br	Cl
cis-2-Methyl	5.7 (**17b**)	46 (**7b**)	
trans-2-Methyl	138 (**17a**)	630 (**7a**)	
2,2-Dimethyl	430 (**24**)		
cis,cis-2,3-Dimethyl	2.2 (**25**)	82 (**10b**)	167 (**11b**)
cis,trans-2,3-Dimethyl	460 (**26**)	9,700 (**12**)	20,000 (**13**)
trans,trans-2,3-Dimethyl	38,000 (**27**)	497,000 (**10a**)	1,330,000 (**11a**)
cis-2,2,3-Trimethyl	83 (**28**)	6,800 (**14b**)	6,700 (**15b**)[d]
trans-2,2,3-Trimethyl	44,700 (**29**)	2,400,000 (**14a**)	4,400,000 (**15a**)
2,2,3,3-Tetramethyl	7,450 (**30**)	1,320,000 (**16**)	

[a] Rates are relative to the parent cyclopropyl derivatives; for data, see footnote *a* in Tables III and IV. [b] Compound numbers are given in parentheses. [c] Reference 1. [d] The extrapolated rate for this compound appears anomalously low, by about a factor of two.

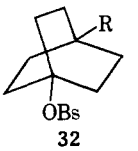
ring opening according to the Woodward–Hoffmann predictions.[3,4] In acetic acid at 100°, the rate enhancement produced by a *trans*-2-methyl substituent relative to the parent cyclopropyl system is (from Table III) a factor of 138 for the tosylates (k_{17a}/k_{21}) and a factor of 630 for the corresponding bromides (k_{7a}/k_{22}). Larger *trans*-2-alkyl substituents (Et, *i*-Pr, *tert*-Bu) increase the rate of acetolysis only slightly more than a methyl substituent, for both tosylates and bromides (Table III). Successive γ-methyl substitution in the *trans*-2-alkylcyclopropyl tosylates (**17a**, **4a**–**6a**) results in inductive stabilization by a rate factor of only about 1.3 per methyl group, *i.e.*, $k_{4a} \simeq 1.3 \times k_{17a}$, $k_{5a} \simeq k_{4a} \times 1.3$, $k_{6a} \simeq 1.3 \times k_{5a} \simeq (1.3)^3 \times k_{17a}$ in acetic acid at 100°; $\rho_{CH_2}^*$ (*vs.* $\sigma_{CH_2}^*$)[17] for γ-methyl substitution in **17a** is −1.25 (100° acetolysis). For the *trans*-2-alkylcyclopropyl bromides (**7a** and **8a**), a similar enhancement in the acetolysis rate of 1.17 for each γ-methyl group can be calculated: $k_{6a} = (1.17)^3 \times k_{5a}$ ($\rho_{CH_2}^* = -0.73$, 100° acetolysis). The small magnitude of these $\rho_{CH_2}^*$ values is seen by a comparison with the values obtained for solvolysis of 3-substituted 1-adamantyl bromides (**31**) and 4-substituted bicyclo[2.2.2]oct-1-yl brosylates (**32**); $\rho_{CH_2}^*$ values for these systems are −2.7 (75°, 80% EtOH) and −2.3 (75°, HOAc), respectively.[18] The small $\rho_{CH_2}^*$ values for α-methyl substitution in the *trans*-2-methylcyclopropyl system seem all the more remarkable because there is substantial delocalization of positive charge to the 2 position in the acetolysis transition states—witness the large rate accelerations for *trans*-2-methyl substitution given above. The effect of *trans*-2-alkyl substituents on cyclopropyl acetolyses is still following the normal inductive order, but is tending toward the Baker–Nathan order (H ≪ Me > Et > *i*-Pr > *tert*-Bu).[19] For unimolecular (SN1) solvolyses, the Baker–Nathan order of alkyl substituent effects was first demonstrated by Hughes, Ingold, and Taher[20] in the ethanolysis and 80% aqueous acetone hydrolysis of the para-substituted benzhydryl chlorides (**33**). Vernon[21] has noted that the Baker–Nathan order appears to be followed for both α- and γ-alkyl substitution in allyl chloride (**34**). The rate



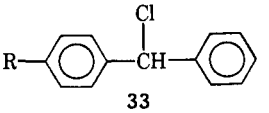
17a, R = CH_3
4a, R = CH_2CH_3
5a, R = $CH(CH_3)_2$
6a, R = $C(CH_3)_3$



31



32



33

(17) (a) R. W. Taft and C. I. Lewis, *J. Amer. Chem. Soc.*, 80, 2436 (1958); (b) C. D. Ritchie, *J. Phys. Chem.*, 65, 2091 (1961).

(18) P. v. R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, 90, 6528 (1968).

(19) (a) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935); *cf.* (b) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; (c) J. March, "Advanced Organic Chemistry: Reactions, Mechanism and Structure," McGraw-Hill, New York, N. Y., 1968, pp 56–57, and references therein.

(20) E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

(21) C. Vernon, *ibid.*, 423 (1954).

accelerations for α-methyl and α-*tert*-butyl substitution are factors of 5670 (k_{35}/k_{34}) and 2520 (k_{36}/k_{34}),

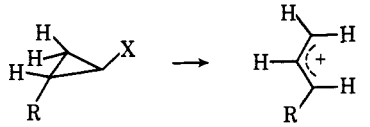
$R_1CH{=}CHCHR_2Cl$

34, $R_1 = R_2 = H$
35, $R_1 = H$; $R_2 = CH_3$
36, $R_1 = H$; $R_2 = C(CH_3)_3$
37, $R_1 = CH_3$; $R_2 = H$
38, $R_1 = C(CH_3)_3$; $R_2 = H$

respectively, in 99.5% aqueous HCOOH at 44.5°; likewise for γ-methyl and γ-*tert*-butyl substitution, rate accelerations of 3550 (k_{37}/k_{34}) and 2260 (k_{38}/k_{34}) are observed under the same conditions.[21] The reasons for the occurrence of the Baker–Nathan or so-called "hyperconjugative" order of alkyl substituent effects in certain systems are still disputed.[19c] Recent molecular orbital calculations indicate that C–C hyperconjugation is more effective than C–H hyperconjugation in stabilizing alkylcarbonium ions.[22] The calculations are consistent with known gas-phase data, which show that β-C–C bonds stabilize carbonium ions to quite a large extent.[23] For example, the reaction $C_2H_5^+ + C_3H_8 \rightarrow n\text{-}C_3H_7^+ + C_2H_6$ is exothermic to the extent of 6.4 kcal/mol. Empirically, the Baker–Nathan order appears to be observed only when the alkyl substituents are attached to a carbon that is initially sp^2 or sp hybridized; when the substituents are attached to a carbon that remains sp^3 hybridized or that undergoes a change from sp^3 to sp^2 hybridization during the reaction being investigated, the normal "inductive" order of alkyl stabilization is observed. The sp^2 hybridization of the exocyclic bonds in the cyclopropane ring[24] may thus account for the fact that a tendency toward Baker–Nathan behavior is observed in the acetolysis of *trans*-2-alkylcyclopropyl derivatives. The tendency of these β-substituent effects in the cyclopropyl system toward the behavior observed for α- and γ-alkyl substituents in the allyl system may be taken as further evidence that the cyclopropyl solvolyses are proceeding through protoallylic transition states.[1]

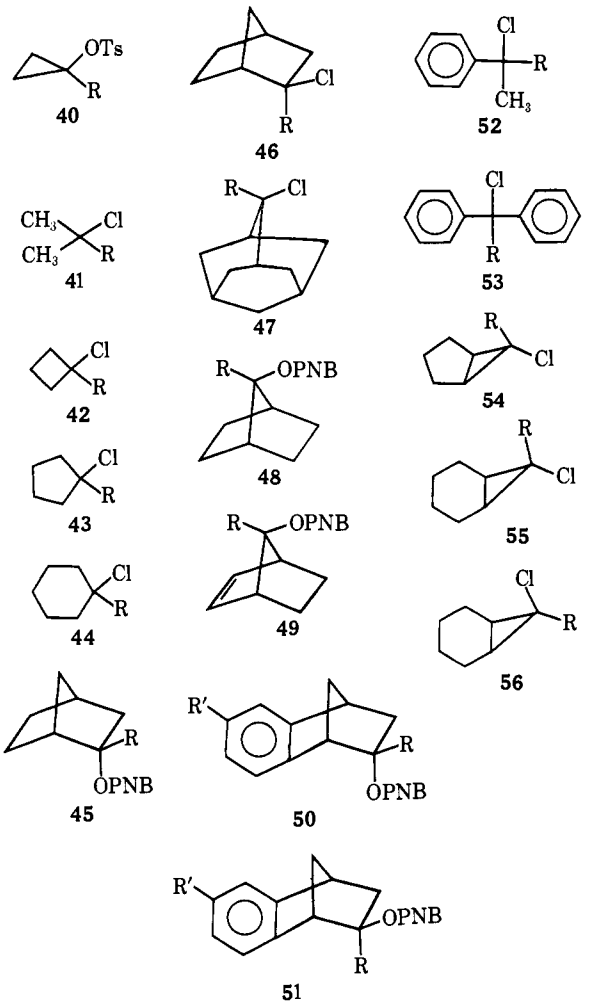
Table IV gives the relative substituent rate accelerations for the two β-substituted cyclopropyl systems where data for all three derivatives (OTs, Br, Cl) are available. The acetolysis rate enhancements relative to the parent cyclopropyl derivatives, are seen to follow the order of leaving groups: Cl > Br > OTs.

It is convenient to divide the substituent effects into electronic and steric categories. For the trans-2 substituted cyclopropyl derivatives additional steric strain due to the 2 substituents should be minimal in both ground and transition states, except for *tert*-butyl substitution. For the *trans*-2-*tert*-butyl cases the steric effects



should at least be independent of the leaving group. The rates of the trans-2 substituted cyclopropyl derivatives in Tables III and IV relative to the parent cyclopropyl derivatives thus can be taken to reflect the electronic stabilization of the protoallylic transition states. The electronic stabilization afforded by β substituents in the cyclopropyl system is thus seen to follow the order of leaving groups: Cl > Br > OTs.

Methyl and Phenyl Substitution Effects. It is interesting to compare the effects of phenyl and methyl substitution in the cyclopropyl system. At 108°, DePuy, *et al.*,[4,10a] found that 1-phenylcyclopropyl tosylate (**39**) and *trans*-2-phenylcyclopropyl tosylate (**3a**, X = OTs) reacted, respectively, 20,000 times and 300 times faster than cyclopropyl tosylate (**21**) on acetolysis. The corresponding rate enhancements for 1-methyl and *trans*-2-methyl substitution in **21** are 313 and 138 in acetic acid at 100°.[1] De Puy also determined ρ^+ values of −4.31 for **39** and −1.75 for **3a** (X = OTs) in acetic acid at 108°.[10a] Considering α substitution first, Table VI gives the data for the cyclopropyl tosylates extrapolated to 25°, along with literature data for other secondary systems (**40–56**). Of particular



interest are the results of Gassman and Fentiman[25] in the *anti*-7-norbornenyl system **49**. The σ^+/ρ^+ plot for **49** (R = Ar) shows a clear break. The ρ^+ value based on the *p*-$N(CH_3)_2$ and *p*-OCH_3 substituents is −4.7,[26] very close to the value of −5.17 observed for **48** (R = Ar) under the same conditions;[27] apparently the stabilization afforded by the α substituent in these two cases is sufficient to completely eliminate participation by the double bond—the 10^{11} rate acceleration due to double bond participation in the parent systems

(22) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970).
(23) F. P. Lossing and G. P. Simeluk, *Can. J. Chem.*, **48**, 955 (1970).
(24) W. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).
(25) See footnote *z*, Table VI.
(26) See second reference of footnote *z*, Table VI.
(27) See Tanida, *et al.*, footnote *g*, Table VI.

Table VI. α-Substitution Effects and Reaction Constants[a,b]

Substrate	Solvent, temp (°C)	k_{CH_3}/k_H	$k_{C_6H_5}/k_H$	ρ^+, R = aryl[c]	Ref
40	HOAc, 25	1.1×10^3	3.9×10^5	−4.31[d]	*n*
41	EtOH, 25	5.5×10^4	2.5×10^6	−4.9, −4.54[e]	*o, p*
42	50% EtOH, 25	1.9×10^2	4.3×10^5	−4.48[e]	*p, q*
43	EtOH, 25	1.8×10^5	6.6×10^8	−4.5, −4.1[e]	*p, r*
44	EtOH, 25	3.3×10^4	6.3×10^6	−4.65[e]	*o, p*
45	80% acetone, 25	1.4×10^5	6×10^8	−3.77	*s*
46	EtOH, 25	6×10^4	3×10^8	−4.3, −3.96[f]	*o, t*
47	80% EtOH, 25	3×10^7	1.6×10^{10}	−4.83[e]	*p, u, v*
48	70% dioxane, 25	9.7×10^7 [g]	4×10^{12}	−5.17, −5.64[e,h]	*p, w, x*
49	70% acetone, 25		1.3×10^3	−4.7,[i] −2.3[j]	*y, z*
50	80% acetone, 25				
	a, R′ = H	3.1×10^4	5.6×10^8	−4.52	*aa–dd*
	b, R′ = OCH_3		6.6×10^8	−4.05	*aa, bb, ee*
51	80% acetone, 25				
	a, R′ = H	1.4×10^4	1.2×10^8	−4.50	*aa–dd*
	b, R′ = OCH_3	3.6×10^3	2.6×10^7	−3.72	*bb, cc, ee, ff*
52	EtOH, 25	1.8×10^3	9×10^4	−4.2[k]	*o, gg*
53	EtOH, 25	3.5×10^2	1×10^4	−2.35[l]	*o, gg*
54	HOAc, 125		$\sim 1.5 \times 10^8$	−4.2[m]	*hh*
55	HOAc, 125		1.5×10^6	−4.2[m]	*hh*
56	HOAc, 125		36	−2.0[m]	*hh*

[a] Necessary extrapolations in this table were made as follows: for changes of solvent an *m* value of 1.0 was assumed for tertiary derivatives; for changes of leaving group the Cl/OTs rate ratio of 1.9×10^{-6} found for the 1-adamantyl system in 80% EtOH at 25° was used for tertiary derivatives (R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971)); for secondary derivatives, the Cl/OTs rate ratio of Brown (8.5×10^{-5} at 25°) (see H. C. Brown and M.-H Rei in Table IV, footnote *a*) was used and for $(k_{OTs,HOAc}/k_{OPNB,\ 80\%\ acetone})_{25°}$ the value of 1.04×10^9 found by Winstein, *et al.* (S. Winstein, M. Shavatsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, **91**, 1548 (1969)) for the *anti*-7-norbornenyl system was employed. [b] OPNB = *p*-nitrobenzoate. [c] *Vs.* σ^+ (H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1948); for a review, see L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963)). [d] At 108°. [e] In 90% aqueous acetone. [f] For the corresponding *p*-nitrobenzoates in 80% aqueous acetone. [g] For the corresponding tosylates in HOAc, extrapolated to 25° (H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967)). [h] For the corresponding chlorides. [i] For *p*-NMe_2 and *p*-OCH_3 substituents on the phenyl ring. [j] For *p*-OCH_3, *p*-H, *p*-CF_3, and *m,m′*-diCF_3 substituents on the phenyl ring. [k] For substituted benzhydryl chlorides. [l] In 60% ether–40% EtOH. [m] At 100°; the correlation is unsatisfactory. [n] References 1 and 10a. [o] Reference 21. [p] H. Tanida and T. Tsushima, *J. Amer. Chem. Soc.*, **92**, 3397 (1970). [q] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951); E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961). [r] H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966). [s] H. C. Brown, M. H. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964); P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968); S. Ikegami, D. L. Van der Jagt, and H. C. Brown, *ibid.*, **90**, 7122 (1968). [t] See Takeuchi and Brown, footnote *s*. [u] See Bingham and Schleyer, footnote *a*. [v] J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970); J. M. Harris, unpublished results. [w] See Winstein, Shavatsky, Norton, and Woodward, footnote *a*. [x] See Tanida, *et al.*, footnote *g*. [y] See Lhomme, Diaz, and Winstein, footnote *a*. [z] P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545, (1969); **92**, 2549 (1970). [aa] H. C. Brown and G. L. Tritle, *ibid.*, **88**, 1320 (1966). [bb] H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968). [cc] J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5907 (1969). [dd] H. C. Brown, S. Ikegami, and K.-T. Liu, *ibid.*, **91**, 5911 (1969). [ee] H. C. Brown and K.-T. Liu, *ibid.* **91**, 5909 (1969). [ff] J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5905 (1969). [gg] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1963, p 41. [hh] D. T. Clark and G. Smale, *Chem. Commun.*, 868 (1969), and private communication.

(k_{49}/k_{48}, R = H)[28] being reduced to a mere factor of 3 in the corresponding α-*p*-anisyl-substituted systems.[29] For less electron-releasing substituents than *p*-OMe on the phenyl ring of **49** (R = C_6H_5), however, the ρ^+ value is only −2.3 and the corresponding k_{49}/k_{48} rate ratios are much higher (42–250,000), indicating that double bond participation in these cases is still present, although reduced in magnitude.[26] This sensitivity of ρ^+ to even moderate amounts of anchimeric assistance gives added significance to the value of −4.2 found for the 1-arylcyclopropyl tosylates. This ρ^+ value is similar to those found for classical tertiary systems (see Table VI) and is similar to the ρ^+ values found for the bicyclic cyclopropyl systems **54** and **55**, geometrically biased against the favored mode of disrotatory ring opening. Acetolyses of **54** and **55** yield ring-closed products of both exo and endo configuration in addition to products of ring opening.[30] On this basis the transition state for acetolysis of **40** (R = C_6H_5) may well resemble a classical, phenyl-stabilized cyclopropyl cation even though the ring-opened 2-phenallyl acetate is the only observed product.[4,10a] The rate enhancement found for 1-phenyl substitution in cyclopropyl tosylate is $10^{5.6}$ (HOAc, 25°), quite low compared with the accelerations of $10^{10.2}$ and $10^{12.6}$ estimated for α-phenyl substitution in the 2-adamantyl (**47**) and 7-norbornyl (**48**) systems. Taking these latter values as "normal" for limiting (k_c) solvolyses in both the secondary (R = H) and tertiary (R = C_6H_5) substrates,[31] the amount of anchimeric assistance in **21** (**40**, R = H) can be estimated to be $10^{4.6}$–$10^{7.0}$ (HOAc, 25°). A similar estimate ($\geq 10^5$) for the anchimeric assistance in **21** is obtained from consideration of the α-methyl substitution effects;[1] in this case, the tertiary 1-methylcyclopropyl tosylate (**40**, R = CH_3) is probably itself accelerated by anchimeric assistance to a small extent.

Considering β-substituent effects, the relative rate accelerations produced by *trans*-β-methyl and *trans*-β-phenyl substituents in the cyclopropyl system are somewhat different than those found for α substitution. Table VII gives the data for the cyclopropyl tosylates (**57**) and bromides (**58**) extrapolated to 25°, as well as literature data for numerous comparison systems. The sen-

(28) See Winstein, Shavatsky, Norton, and Woodward, footnote *a*, Table VI.

(29) See first reference of footnote *z*, Table VI.

(30) See footnote *hh*, Table VI.

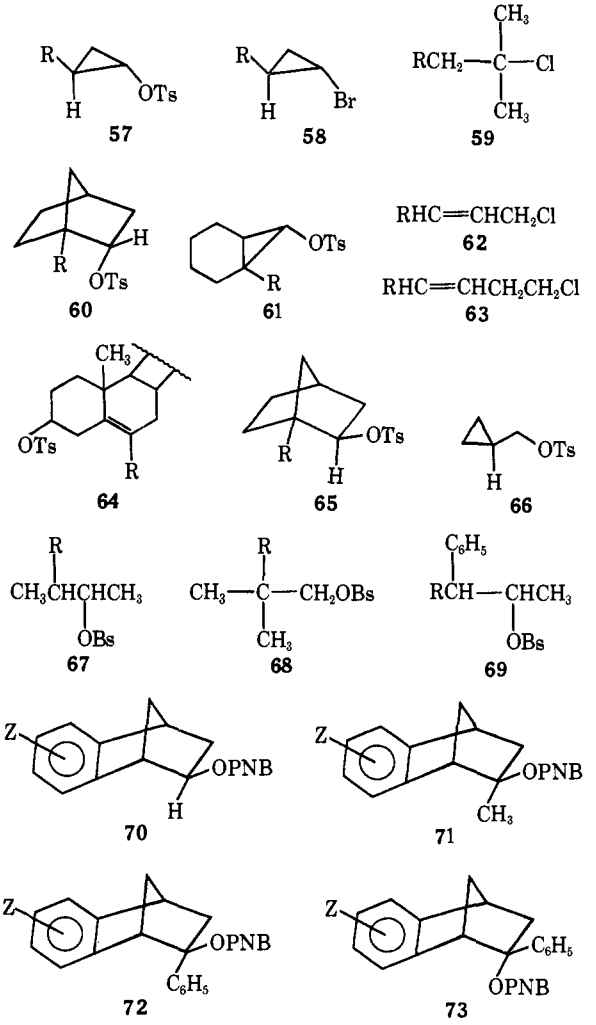
(31) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

Table VII. Substitution Effects and Reaction Constants

Substrate	Solvent, temp (°C)	k_{CH_3}/k_H	$k_{C_6H_5}/k_H$	ρ, R = aryl[a]	Ref
57	HOAc, 25	320	510	−2.35,[b] −1.75[b-d]	*l*
58	HOAc, 25	1300	9400		*m*
59	80% EtOH, 40.8	1.65	0.17	−1.11	*n*
60	HOAc, 75	1.17	0.56	−1.02, −0.69[c,d]	*o*
61	HOAc, 150	3.9	9.3		*p*
62	99.5% HCOOH, 44.6	3550	$\sim 5 \times 10^5$		*q*
63	HCOOH, 50	210	96		*r*
64	90% dioxane, 50	75	0.3	−0.96, 0.71[c,e]	*s*
65	HOAc, 25	53	4.2	−1.36, −0.95[c,d]	*o*
66	HOAc, 25	4.7	1.7		*t*
67	HOAc, 49.6	3.0	0.64	−2.4[c,f]	*u, v*
68	HOAc, 74.7	0.1	24	−2.96[c]	*v–x*
69	HOAc, 74.8	4.5	6.0	−2.0,[g,h] −4.2[g,i]	*v, w, y*
70	HOAc, 77.6			−3.26,[c] −2.71[c,j,k]	*z, aa*
71	50% acetone, 125			−1.9[c]	*bb*
72	80% acetone, 25			−0.9[c,k]	*cc*
73	80% acetone, 25			−0.2[c,k]	*cc*

[a] σ. [b] At 108°. [c] *Vs.* σ^+. [d] The correlation is better with σ than with σ^+. [e] Neither correlation is appreciably better. [f] At 25°. [g] For 2,2-diphenylethyl tosylate in HOAc at 99.5°. [h] For substitution on the nonmigrating phenyl group. [i] For substitution on the migrating phenyl group. [j] For the corresponding chloride in 80% acetone at 25°. [k] Correlation based on only two points. [l] References 1 and 10a. [m] Reference 10c. [n] A. Landis and C. A. Vander Werf, *J. Amer. Chem. Soc.*, **80**, 5277 (1958). [o] D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960. [p] Reference 3. [q] Reference 21. [r] K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965). [s] R. A Sneen, *ibid.*, **80**, 3977, 3982 (1960). [t] D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964). [u] C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4289 (1969). [v] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952). [w] R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957). [x] E. N. McElrath, R. M. Fritz, C. Brown, C. Y. Le Gall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960). [y] S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Amer. Chem. Soc.*, **74**, 1140 (1952). [z] See Table VI, footnote *bb*. [aa] H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Amer. Chem. Soc.*, **91**, 4512 (1969). [bb] See Table VI, footnote *ff*. [cc] See Table VI, footnote *cc*.

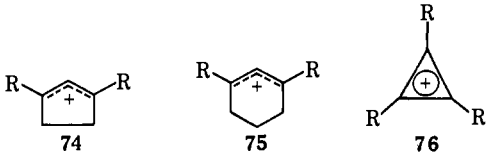
sitivity of ρ and ρ^+ constants to charge delocalization is again illustrated by **59–73** in this table. The rate enhancement (25°, HOAc) produced by *trans*-β-methyl substitution in cyclopropyl tosylate (**57** in Table VII) is smaller than that for α-methyl substitution (**40** in Table VI) by less than a factor of four. For phenyl substitution, however, the trans-β-substitution effect is smaller than that for α substitution by a factor of $10^{2.9}$ under the same conditions. This is true even though the ρ^+ value for **57** (R = C_6H_5) is −1.75,[10a] showing considerable charge delocalization to the β position in the acetolysis transition state. The lower β-phenyl substitution effect can be attributed to the rate-retarding inductive effect of the phenyl substituent (see **59** and **60** in Table VII).[32] When attached directly to a center of developing positive charge, the adverse inductive effect of a phenyl substituent is more than compensated by the extremely favorable benzyl-type resonance and an α-phenyl group is thus more effective in stabilizing a developing cationic center than an α-methyl group (Table VI). For β or more remote substitution (Table VII), however (except for such cases as γ substitution in the allyl system (**62**) where the positive charge is transmitted directly to the site of attachment by conjugative resonance), the combined favorable inductive and hyperconjugative effects of the methyl substituents become dominant. Indeed, the experimental evidence of Table VII shows that the ability of a phenyl group to stabilize by resonance a charge-delocalized transition state, as is found in participating systems, is at best equivalent to that of a methyl group and is often much less. In stabilizing delocalized ions themselves in strong acid media, alkyl groups have also been found to be superior to phenyl substituents in the cyclopentenyl (**74**),[33] cyclohexenyl (**75**),[33] and cyclopropenyl (**76**)[34] cations. Dewar[35] has provided a



(32) (a) J. E. Norlander and W. E. Deadman, *J. Amer. Chem. Soc.*, 90, 1590 (1968), footnote 27; (b) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4294, 4296 (1969).

(33) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, 87, 4533 (1965).

(34) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, 84, 3168 (1962).



74 75 76

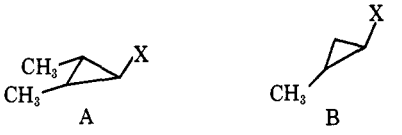
justification of this behavior on theoretical grounds. We conclude that methyl rather than phenyl substituents should be used when probing for nonclassical charge delocalization in systems suspected of participation. For the cyclopropyl system itself, the large β-substituent effects (particularly for phenyl substituents) and the large ρ^+ value for **57** (R = aryl C_6H_5) again serve to emphasize the protoallylic nature of the acetolysis transition states of secondary cyclopropyl derivatives.

The Degree of Ring Opening at the Transition State for Various Cyclopropyl Derivatives. The magnitude of *trans*-β substituent effects in the cyclopropyl system follows the leaving group order: Cl > Br > OTs. One plausible explanation for this dependence would be that the transition states for solvolysis of cyclopropyl halides were occurring after a greater degree of ring opening than those for the corresponding tosylates. Were this the case, greater charge delocalization to the β positions in the transition states for the halides would be expected and, hence, larger β-substituent effects. A close examination of the results for alkyl-substituted cyclopropyl tosylates and bromides suggests, however, that this explanation is not valid.

The *trans,trans*-2,3-dimethylcyclopropyl derivatives (**10**a, **11**a, **27**) suffer from steric crowding of the *cis*-methyl groups in the ground state;[36] this interaction should be independent of the trans leaving group. Since these methyl groups rotate outward (*i.e.*, move apart) in the favored mode of disrotatory opening, compounds **10**a, **11**a, and **27** should be accelerated in rate due to relief of this ground-state steric strain. The magnitude of this acceleration should be a measure of the degree of ring opening at the transition state.

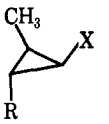
The steric contribution to the rate of a *trans,trans*-2,3-dimethylcyclopropyl derivative can be evaluated from eq 1. Since the "electronic" stabilization afforded by a β-methyl substituent depends on both the leaving group and the number of β substituents already present, the second term on the right of eq 1 is best approximated

$$k_A = k_B \times (\text{"electronic" } \beta\text{-methyl stabilization factor}) \times (\text{steric strain release factor}) \quad (1)$$



A B

by the rate ratio k_{78}/k_{77} for the particular leaving group being considered. As steric contributions to both rates in this ratio should be similar, the ratio should accurately reflect the "electronic" stabilization provided



77, R = H
78, R = CH_3

by a second β-methyl substituent. For *trans,trans*-2,3-dimethylcyclopropyl tosylate (**27**), eq 1 becomes

$$k_{27} = k_{17a} \times (k_{26}/k_{17b}) \times (\text{strain relief factor})$$

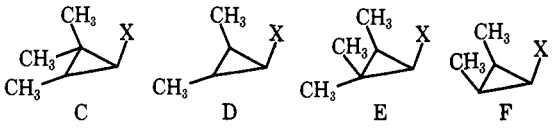
and the calculated strain relief factor (100°, HOAc) is 3.32. For *trans,trans*-2,3-dimethylcyclopropyl bromide (**10**a), eq 1 becomes

$$k_{10a} = k_{7a} \times (k_{12}/k_{7b}) \times (\text{strain relief factor})$$

and the calculated strain relief factor is 3.66 under the same conditions.

Ground-state steric crowding of *trans*-β-methyl groups is also present in the *trans*-2,2,3-trimethylcyclopropyl derivatives (**14**a, **15**a, and **29**). We can evaluate the steric acceleration in rate due to relief of this interaction in the transition state from eq 2. The second term on the right of eq 2 now approximates the "electronic" stabilization of a third β-methyl substituent. For *trans*-2,2,3-trimethylcyclopropyl tosylate (**29**) eq 2

$$k_C = k_D \times (k_E/k_F) \times (\text{steric strain release factor}) \quad (2)$$



C D E F

becomes

$$k_{29} = k_{26} \times (k_{28}/k_{25}) \times (\text{strain relief factor})$$

while for the corresponding bromide (**14**a) we get

$$k_{14a} = k_{12} \times (k_{14b}/k_{10b}) \times (\text{strain release factor})$$

The calculated strain release factors are 2.55 and 2.95 for the tosylate and bromide, respectively, in HOAc at 100°.

Given the small differences in these calculated strain release factors and the nature of the nonbonded interaction potential (proportional to $1/r^{12}$)[38] it would appear that changes in the degree of ring opening at the transition state for similarly substituted cyclopropyl tosylates and bromides are too small to be responsible for the observed dependence of substituent effects on the leaving group (Tables III–V).[39]

Another possible explanation for the results of Tables III–V is that the substitution effect differences for different leaving groups are due to changes in the overall amount of positive charge on the cyclopropyl moiety at the transition state.[40] We distinguish here between the *amount* of overall charge, which depends on the degree of C–X bond breaking, and the *distribution* of that charge between the α- and β-carbons (considered above). This explanation would be in accord with the Hammond postulate[40]—greatest progress along the reaction coordinate at the transition state for the

(35) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, 16, 321 (1965); see especially p 330.

(36) The enthalpy difference between *cis*-1,2-dimethylcyclopropane and its more stable trans isomer is 1.1 kcal/mol;[37] at 100° relief of 1.1 kcal/mol in ground-state strain energy would produce a steric acceleration of 4.5 in rate.

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

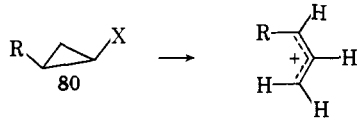
(38) K. Mislow, *Top. Stereochem.*, 38 (1965).

(39) The similarity of alkyl substituent effects for the cyclopropyl bromides and chlorides (Table V) suggests that this conclusion may be extended to include the chlorides as well.

(40) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 344 (1955).

poorest leaving group. It would also require that α- and β-substituent effects in the cyclopropyl system follow the same leaving group order. The experimental evidence on this last point is inconclusive. Roberts, *et al.*, found that 1-methylcyclopropyl bromide (**79**) solvolyzed 40 times faster than cyclopropyl bromide (**22**) in 50% aqueous EtOH at 130°. The acetolysis rate enhancement for 1-methyl substitution in cyclopropyl tosylate (**21**) is a factor of 210 at 130°.[1] The latter effect, however, when corrected for the difference in solvents (compare **7a** and **19a** in Table III) is reduced to a factor of ~120. Furthermore, we now believe that the steric acceleration in going from a secondary system to a tertiary system is much greater for the tosylate derivatives than for the corresponding bromides.[41] Thus, if all steric factors could be accurately evaluated, the "electronic" rate enhancement provided by an α-methyl substituent might well be greater for cyclopropyl bromide than for the tosylate.

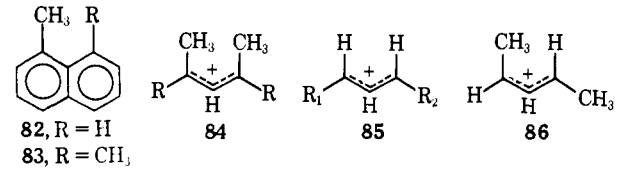
Steric Effects in Cis-β-Substituted Cyclopropyl Derivatives. In analyzing the kinetic results for trans-2-substituted cyclopropyl derivatives steric effects due to the β substituent were considered to be unimportant. The *trans*-2-alkylcyclopropyl tosylates (**17a**, **4a**–**6a**) show a fairly regular progression in rate (Table III) as would be predicted on "electronic" grounds (*vide supra*). The corresponding cis-substituted tosylates (**17b**, **4b**–**6b**) show no such regularity in their observed reactivity, particularly **6b**, and they are much less reactive than their trans counterparts although "electronic" effects might well be expected to be similar for isomeric derivatives.[42] The favored mode of disrotatory ring opening for a cis-2 substituted cyclopropyl derivative **80** leads to a sterically crowded allyl cation **81** with an



80 **81**

"interior" substituent. It is this steric crowding in the transition states for solvolysis of cis-β-substituted cyclopropyl derivatives that is responsible for the large trans/cis rate ratios of Table III.

Initially[1,11] we used the allyl cation intermediates expected for stereospecific, disrotatory opening to approximate the strain energy differences in the acetolysis transition states for **24**–**30**. The strain in **81** (R = CH_3) was taken to be 1.6 kcal/mol based on a strain estimate for the best available model, 1-methylnaphthalene (**82**).[45] This value, although somewhat larger than other strain estimates for **82** based on more direct determinations,[46] was chosen for consistency since the same investigation provided the only estimate of the



82, R = H
83, R = CH_3
84 **85** **86**

strain in 1,8-dimethylnaphthalene (**83**). This latter value, 7.6 kcal/mol,[45] was used to approximate the strain in the *cis,cis*-dimethallyl cation (**84**, R = H). "Exterior" allyl cation substituents (R = alkyl in **84**) were considered sterically negligible; **85** (R_1, R_2 = H alkyl) was considered to be strain free.

The experimental trans/cis rate ratio for the isomeric 2-methylcyclopropyl tosylates (**17**) in acetic acid at 150° is k_{17a}/k_{17b} = 21.[1] This corresponds to a transition-state free-energy difference of 2.56 kcal/mol between the isomers, assuming ground-state strains are equal. If there is significant ground-state steric strain in **17b** due to tosyl-methyl crowding which can be relieved in going to the transition state, the transition-state free-energy difference will be even greater. This suggests to us that the relievable ground-state steric strain due to cis crowding in **17b** is small.

We would expect the steric factors influencing the reactivity of the *cis*- and *trans*-2-ethylcyclopropyl tosylates (**4**) and 2-isopropylcyclopropyl tosylates (**5**) to be similar to those in the 2-methylcyclopropyl tosylates (**17**), since the effective steric size of these three alkyl groups should nearly be the same. This is borne out experimentally—the observed trans/cis rate ratios for **4** and **5** both being 21 (150°, HOAc), the same value as found for **17**. From these experimental results, the original estimate of 1.6 kcal/mol for the strain in **81** (R = CH_3) appears somewhat low. This conclusion is confirmed by the results of Saunders, *et al.*,[47] who generated the isomeric 1,3-dimethylallyl cations directly in SO_2ClF–SbF_5 from **11** and **13**, and observed their equilibration. They found that **86** isomerized cleanly to the presumably strain-free **85** (R_1 = R_2 = CH_3) at 35°. Assuming an nmr detectability limit of ≥5%, the strain energy for **86** (and for **81**, R = CH_3) is then ≥1.8 kcal/mol. Activation energies for the conversions **84** (R = H) → **86** and **86** → **85** (R_1 = R_2 = CH_3) of 17.5 and 24.0 kcal/mol, respectively, were also determined. Since the former transition state and **86** should have comparable strain energies, one expects 6.5 kcal/mol in ΔH (4.4 kcal/mol in ΔF) as the strain-energy difference between **84** (R = H) and **86**. This figure is in good agreement with the 6.0 kcal/mol (ΔH) difference predicted by the naphthalene models.

Of special interest is the observed reactivity of the *cis*-2-*tert*-butylcyclopropyl derivatives **6b** and **8b**. We would expect large decreases in rate for these derivatives, based on the presumably high strain energy of **81** (R = *tert*-C_4H_9). While *cis*-2-*tert*-butylcyclopropyl tosylate (**6b**) is slightly less reactive (Table III) than *cis*-2-methylcyclopropyl tosylate (**17b**), this decrease in reactivity (k_{6b}/k_{17b} = 0.86) is less than a factor of 3

(41) See Bingham and Schleyer, Table VI, footnote *a*.

(42) Based on a CNDO II–SCF analysis of the cyclopropyl cation → allyl cation transformation, Clark and Smale[43] have suggested that the "electronic" stabilization provided by trans β substituents in the cyclopropyl system may be somewhat larger than that of their cis counterparts for large degrees of ring opening. As Clark and Armstrong[44] did not repeat this suggestion in reporting later *ab initio* calculations on the same transformation, and as no β-substituted cyclopropyl systems were explicitly calculated, the possibility of differing cis and trans "electronic" effects remains an open question. A reasonable experimental test of this hypothesis would perhaps be to determine solvolytic ρ^+ values for substitution in the *cis*- and in the *trans*-phenyl groups of a 2,2-diphenylcyclopropyl system.

(43) D. T. Clark and G. Smale, *Tetrahedron*, **25**, 13 (1969).

(44) D. T. Clark and D. A. Armstrong, *Theoret. Chim. Acta*, **13**, 365 (1969).

(45) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

(46) (a) G. Suld and A. P. Stuart, *J. Org. Chem.*, **29**, 2939 (1964); (b) D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).

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

Table VIII. Relative Acetolysis Rates of 2,3-Dimethylcyclopropyl Derivatives

Leaving group	Stereochemistry of β-methyl substituents[a]				
	Trans,trans	Cis,cis		Cis,trans	
	k_{ttrel}	k_{ccrel}	(k_{ccrel}/k_{ttrel})	k_{ctrel}	(k_{otrel}/k_{ttrel})
OTs[b]	(**27**) 1.0[c]	(**25**) 1.0[d]	1.0	(**26**) 1.0[e]	1.0
Cl	(**11a**) 0.015	(**11b**) 0.033	2.2	(**13**) 0.017	1.1
Br	(**10a**) 0.49	(**10b**) 1.4	2.8	(**12**) 0.78	1.6

[a] Compound numbers are given in parentheses. [b] Reference 1. [c] $k_1 = 1.59 \times 10^{-3}$ sec^{-1}. [d] $k_1 = 9.0 \times 10^{-8}$ sec^{-1}. [e] $k_1 = 1.93 \times 10^{-5}$ sec^{-1}.

when compared to the relative reactivity of the corresponding trans isomers ($k_{6a}/k_{17a} = 2.4$). Moreover, *cis*-2-*tert*-butylcyclopropyl bromide (**8b**) actually reacts two times *faster* than *cis*-2-methylcyclopropyl bromide (**7b**), which relative reactivity is slightly greater than that found for the corresponding trans isomers ($k_{8a}/k_{7a} = 1.7$). We attribute the relatively high reactivity of **6b** and **8b** to the relief of ground-state steric strain. Apparently relief of *tert*-butyl leaving group ground-state steric crowding nearly compensates for the increase of strain in the transition state caused by inward rotation of the *tert*-butyl group of **6b**. For the corresponding *cis*-2-*tert*-butylcyclopropyl bromide (**6b**), the ground-state strain relief actually appears to be greater than the strain increase in going to the transition state. The dependence of ground-state steric strains in cis-β-substituted cyclopropyl systems on the leaving group is discussed in the following section.

Leaving Group Steric Differences in Cyclopropyl Systems. We believe that the substituent strain in a cis-β-substituted cyclopropyl derivative may increase by as much as 1.3 kcal/mol in going from a tosylate leaving group to the corresponding bromide. This can best be seen by comparing trans/cis rate ratios for a given β substituent with different leaving groups. Such isomeric rate ratio comparisons should eliminate by cancellation "electronic" substituent effect differences due to changes in the leaving group. Moreover, steric factors should be minimal for the trans derivatives, and assuming any leaving group steric interactions are completely relieved, transition-state strains for a given cis substituent will not vary appreciably with the leaving group. (The degree of ring opening at the transition state for a given cyclopropyl system does not appear to change significantly with different leaving groups.) Thus, different isomeric rate ratios observed for a given β-substituted cyclopropyl system should primarily reflect differences in ground-state steric strains of the cis isomers; the greater the strain in the cis isomer, the lower the trans/cis rate ratio should be for that leaving group.

Experimentally (Tables III and IV), the trans/cis rate ratios observed for 2-substituted cyclopropyl tosylates are always higher than those found for the corresponding bromide derivatives. This indicates a larger effective steric size for the bromide leaving group than for the tosylate in these cyclopropyl systems. Furthermore, the trans/cis rate ratios show more variation with the leaving group for larger 2 substituents. Thus, in the 2-methylcyclopropyl system (Table III), the trans/cis rate ratios are 24 for the tosylates (**17**) and 14 for the bromides (**7**); this suggests *cis*-2-methylcyclopropyl bromide (**7b**) to be only slightly more strained (0.4 kcal/mol) than the corresponding *cis*-tosylate **17b**. In the 2-phenylcyclopropyl system, however, with its sterically larger phenyl group, the observed trans/cis rate ratio is 20 for the tosylates **3** (X = OTs) and only **4** for the bromides **3** (X = Br). Based on these isomeric rate ratios the strain difference between the *cis*-bromide **3b** (X = Br) and the *cis*-tosylate **3b** (X = OTs) is 1.2 kcal/mol.

The largest leaving group differences for any monosubstituted cyclopropyl system are observed in the 2-*tert*-butylcyclopropyl system, with its very bulky alkyl substituent. The trans/cis rate ratios for this system (Table IV) vary from 66 for the tosylates (**6**), to 26 for the chlorides (**9**), to only 11 for the bromides (**8**). According to our interpretation, the low isomeric reactivity ratio for the bromides indicates that *cis*-2-*tert*-butylcyclopropyl bromide (**8b**) is 1.3 kcal/mol more strained than the corresponding *cis*-tosylate **6b**, whose ground-state substituent strain is probably already high (see preceding section). The kinetic results in the 2-*tert*-butylcyclopropyl system indicate the order of leaving group steric size to be Br > Cl > OTs.

Further insight into these leaving group steric differences can be obtained by considering the relative rates of tosylates, chlorides, and bromides in the 2,3-dimethylcyclopropyl system (Table VIII).[47a] For the *trans,trans*-2,3-dimethylcyclopropyl derivatives, the relative reactivity of the three leaving groups is OTs = 1.00, Cl = 0.015, and Br = 0.49. As both ground and transition strains for these trans,trans derivatives should be independent of the leaving group, we take these results as giving the "electronic" leaving group relative reactivities in the 2,3-dimethylcyclopropyl system. The *cis,cis*-2,3-dimethylcyclopropyl derivatives, whose ground-state strains depend on the leaving group, exhibit the relative reactivities OTs = 1.0, Cl = 0.033, and Br = 1.4, quite different from the relative reactivities displayed by the trans,trans derivatives. Comparing relative tosylate–halide reactivities (column 3 of Table VIII), the cis,cis-chloride **11b** and *cis,cis*-bromide **10b** are, respectively, 2.2 and 2.8 times more reactive relative to the *cis,cis*-tosylate **25** than are the corresponding *trans,trans*-halides **11a** and **10a** relative to **27**. We attribute the enhanced relative reactivity of the *cis,cis*-halides **11b** and **10b** to the presence of greater ground-state steric strain in these molecules than is present in **25**. While it is impossible from our data to assess accurately the *absolute* substituent strains present in these *cis,cis*-2,3-dimethylcyclopropyl derivatives, the original, empirical estimate of 1.7 kcal/mol for the substituent strain in **25** seems reasonable.[1,11] We take the results in Table VIII to indicate, however, that *cis,cis*-2,3-dimethylcyclopropyl chloride (**11b**) and bromide (**10b**) are *relatively* 0.6 and 0.8 kcal/mol more

(47a) NOTE ADDED IN PROOF. The steric hindrance between *cis*-cyclopropyl substituents is shown by a recent X-ray structure (W. Saenger and C. H. Schwalbe, *J. Org. Chem.*, 36, 3401 (1971).

strained, respectively, than the corresponding tosylate **25**. Leaving group steric differences are also seen in the relative reactivities of the *cis,trans*-2,3-dimethylcyclopropyl derivatives (OTs = 1.0, Cl = 0.017, Br = 0.78), although ground-state steric crowding in these molecules is much less severe than in the cis,cis isomers. Comparing tosylate–halide relative reactivities to those of the trans,trans isomers (column 5 of Table VIII), a very slight reactivity increase (1.1) for *cis,trans*-2,3-dimethylcyclopropyl chloride (**13**) and a somewhat larger enhancement (1.6) for the corresponding bromide **12** is found. Both the magnitude and the direction of the observed effects are in accord with our steric explanation. If the relative reactivity increase of **12** is attributed entirely to ground-state steric effects, the strain difference between **12** and **26** is calculated to be 0.35 kcal/mol, in good agreement with the 0.4-kcal/mol strain difference between *cis*-2-methylcyclopropyl bromide (**7b**) and the corresponding tosylate **17b** estimated from trans/cis rate ratios. As in the 2-*tert*-butylcyclopropyl system, the leaving group steric size order in the 2,3-dimethylcyclopropyl system is Br > Cl > OTs.

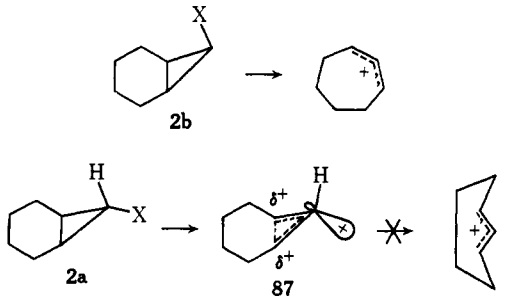
Ground-state steric factors similar to those affecting the relative reactivities of *cis,cis*-2,3-dimethylcyclopropyl derivatives should also influence the reactivities of endo derivatives in the 7-norcaryl system (Table IX).

Table IX. Relative Rates and Isomeric Rate Ratios for 7-Norcaryl Derivatives[a]

Leaving group	k_{rel}, exo	k_{rel} endo	k_{endo}/k_{exo}
OTs	1.0[b]	1.0[c]	94.5
Cl	~0.0016	0.045	2,800
Br	~0.0027	1.27	46,500
OTf[d]	4000	815	20.5

[a] In acetic acid at 200°. [b] $k_1 = 2.67 \times 10^{-4}$ sec^{-1}. [c] $k_1 = 2.52 \times 10^{-2}$ sec^{-1}. [d] Trifluoromethanesulfonate (triflate).

In this bicyclic cyclopropyl system the endo isomers **2b** are free to undergo the favored mode of disrotatory opening while the exo isomers **2a** are geometrically constrained against complete opening by the favored mode and are postulated to go only to a "half-opened" intermediate **87**.[5a] Thus, endo/exo rate ratios in this



system are greater than unity, and relief of ground-state strain in the endo isomers should serve to *raise* the isomeric rate ratios, rather than to *lower* them as was the case in monocyclic systems. Inspection of Table IX shows that the endo/exo rate ratios in the 7-norcaryl system are enormously dependent on the leaving group, varying by more than a factor of 2000 in going from the triflates (k_N/k_X = 20.5) to the bromides (k_N/k_X = 46,500). Nevertheless, comparison of the relative reactivities for the endo derivatives (OTs = 1.0, Br = 1.3, Cl = 0.045) with those found for the *cis,cis*-2,3-dimethylcyclopropyl derivatives (column 2 of Table VIII) suggests that steric differences due to the leaving group are indeed similar in the two systems. (Note particularly that the bromide derivatives in both systems are more reactive than the corresponding tosylates; we believe the causes of this inverted reactivity are definitely steric in origin.) Leaving group steric differences thus contribute to but cannot completely explain the extreme dependence of isomeric rate ratios in the 7-norcaryl system on the leaving group. This problem will be discussed more fully in a forthcoming paper dealing with bicyclic cyclopropyl derivatives.

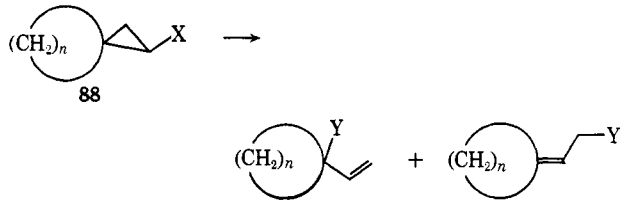
Leaving group steric differences can also be used to explain the results of kinetic studies on some spirocyclopropyl systems (Table X). The *p*-nitrobenzene-

Table X. Relative Solvolysis Rates of Spirocyclopropyl Derivatives

Compd	k_{rel}, HOAc, 95° X = ONs[a]	k_{rel} 50% EtOH, 95°[b] X = Br	X =
88, n = 3	1.0[c]	1.0[d]	1.0[e]
88, n = 4	0.82	1.71	1.59
88, n = 5	0.43		
88, n = 6	0.85		
89, 2,2-dimethylcyclopropyl	0.38		

[a] Extrapolated from ref 48. [b] From Table IV, Landgrebe and Applequist, footnote *a*. [c] $k_1 = 2.83 \times 10^{-4}$ sec^{-1}. [d] $k_1 = 6.36 \times 10^{-4}$ sec^{-1}. [e] $k_1 = 1.3 \times 10^{-5}$ sec^{-1}.

sulfonates in this table were studied by Lazarus[48] in acetic acid, while the corresponding halides were solvolyzed in 50% aqueous ethanol by Landgrebe and Applequist.[49] The solvolysis products in each case were a mixture of the expected allyl derivatives[48,49]



Assuming the "electronic" effects to be about equal in all cases, the spiro[2.3]hex-1-yl derivatives (**88**, n = 3) would be expected to react faster than either the corresponding spiro[2.4]hept-1-yl derivatives (**88**, n = 4) or the monocyclic 2,2-dimethylcyclopropyl derivatives **89**, because the overall relief of angle strain in going from the cyclopropyl ground state (preferred $\theta \sim$ 116–118°)[50] to the protoallylic transition state (preferred θ = 115.3°)[51] should be greatest for the spirohexyl derivatives (**88**, n = 3) in which the cyclobutyl ring would prefer $\theta \approx 90°$. This is the order of re-

(48) S. Lazarus, Ph.D. Thesis, Seton Hall University, 1967.
(49) See Landgrebe and Applequist, Table IV, footnote *a*.
(50) (a) O. Bastiansen and O. Hassel, *Tidsskr. Kjemi Bergv. Met.*, 6, 71 (1946); (b) H. Pfeiffer, Ph.D. Thesis, California Institute of Technology, 1948; (c) R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.* 40, 1022 (1964); (d) O. Bastiansen and A. de Meijere, *Acta Chem. Scand.*, 20, 516 (1966).
(51) Using isobutylene as a model: V. W. Laurie, *J. Chem. Phys.*, 39, 1732 (1963).

activity observed for the arenesulfonates **88**, X = ONs, and **89**. As ground-state steric crowding should increase in going from the spirohexyl to the spiroheptyl derivative (the methylene group cis to the leaving group is held "back" less in the five-membered ring than in the four-membered ring), Lazarus' results provide support for our assumption of negligible steric crowding between a tosylate and a *cis*-methyl group in a cyclopropane ring. For the spirocyclopropyl *halides*, however, the spiroheptyl derivatives (**88**, $n = 4$) react *faster* than the spirohexyl derivatives (**88**, $n = 3$). If ground-state steric strain in the halide derivatives (**88**, X = Cl or Br) is larger than in the corresponding tosylates (**88**, X = OTs), the increased steric crowding in the spiroheptyl ground states could be accelerating these halides and reversing the relative reactivity found for the corresponding nosylates. If this explanation is correct, the steric size of the leaving groups again follows the order Br > Cl > ONs (≈ OTs).

It is difficult to assess the steric size of groups in organic molecules, since the effective size will depend on the situation. Thus, van der Waals' radii bear little relationship to conformational ΔG values for axial–equatorial equilibria in the cyclohexyl system.[52] The 1–3 interactions in an axial cyclohexane derivative are with hydrogens; due to the short C–H bond length (1.09 Å) the relative position of the interacting atoms changes significantly with the C–X bond length, the effective size of the substituent becoming smaller as r_{C-X} increases. In the cis-β-substituted cyclopropyl systems considered above, however, the relative position of the interacting *cis*-alkyl and leaving groups changes little in going from a tosylate ($r_{C-O} \approx 1.4$ Å) to the corresponding bromide ($r_{C-Br} \approx 1.9$ Å). Thus, it is not surprising that the order of leaving group steric size found in these systems parallels the van der Waals' radii: Br (1.95 Å) > Cl (1.8 Å) > O (1.4 Å).[53,54]

Conclusions

The magnitude of alkyl substituent effects in the cyclopropyl system follows the order of leaving groups: Cl > Br > OTs. These differences do not appear to be due primarily to differences in the degree of ring opening at the transition state for the various derivatives. Significant steric differences in the various leaving groups are observed in cyclopropyl systems having cis-β substituents. The effective steric size of the various leaving groups follows the order: Br > Cl > OTs.

Experimental Section

For general remarks see the preceding paper.[1] Spinning band distillations were performed on Nester/Faust annular spinning band distillation columns (Models NF-175 and NFT-50).

Alkyl-Substituted Cyclopropyl Tosylates. The general method of Schöllkopf, *et al.*, was used, as described previously;[1,11] experimental details will not be repeated here.

2-Chloroethyl 2-Ethylcyclopropyl Ether. Dichloromethyl 2-chloroethyl ether[55] (58.0 g, 0.36 mol) was treated with specially prepared methyllithium[1] in the presence of an excess of 1-butene (Matheson, C.P. grade) at 0° to give 27.3 g (51%) of product: bp 86–88° (40 mm); nmr (CCl_4) τ 6.2–7.2 (m, 5 H), 8.3–9.9 (m, 8 H). On the basis of a distinguishable resonance at τ 7.02, assigned to the α proton on the cyclopropyl ring in the trans isomer, the cis/trans isomeric product ratio was estimated as *ca.* 3/1.

2-Ethylcyclopropanol. 2-Chloroethyl 2-ethylcyclopropyl ether (20.0 g, 0.135 mol) was treated with *n*-butyllithium in hexane (Foote) to give 10.0 g (86%) of product: bp 60–62° (40 mm); nmr (CCl_4) τ 6.00 (s, 1, O*H*), 6.60 (m, 0.75, C*H*OH cis), 6.93 (m, 0.25, C*H*OH trans), 8.2–10.0 (m, 8 H). The isomeric product ratio was cis/trans ≈3/1 by nmr.

***trans*-2-Ethylcyclopropyl Tosylate (4a) and *cis*-2-Ethylcyclopropyl Tosylate (4b).** The normal pyridine procedure was employed.[56] 2-Ethylcyclopropanol (7.0 g, 0.08 mol) and freshly recrystallized tosyl chloride (20.0 g, 0.105 mol) gave 12.2 g (64%) of a mixture of liquid isomeric **4**: nmr (CCl_4) τ 2.46 (AB q, 4 H, C_6H_4), 6.04 (d of t, 0.8 H, $J_d = 3$ Hz, $J_t = 6$ Hz, C*H*OTs cis), 6.36 (m, 0.2 H, C*H*OTs trans), 7.58 (s, 3 H, $-C_6H_4CH_3$), 8.4–9.8 (m, 8 H).

Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.90; H, 6.64.

The pure cis isomer **4b** was isolated after preparative solvolysis in buffered acetic acid. Heating 7.2 g of the mixture **4** at 125° for 18 hr gave 2.6 g (~45%) of liquid **4b**: nmr (neat) τ 2.45 (AB q, 4 H, C_6H_4), 6.01 (d of t, 1, $J_d = 3$ Hz, $J_t = 6$ Hz, C*H*OTs), 7.69 (s, 3 H, $C_6H_6CH_3$), 8.4–9.8 (m, 8 H).

2-Chloroethyl 2-Isopropylcyclopropyl Ether. Dichloromethyl 2-chloroethyl ether[55] (58 g, 0.36 mol) was treated with methyllithium in the presence of an excess of 3-methyl-1-butene (Matheson, C.P. grade) at 0° to give 30.1 g (57%) of product: bp 92–94° (40 mm); nmr (CCl_4) τ 6.1–7.2 (m, 5 H), 8.4–10.0 (m, 10 H). The isomeric product ratio was cis/trans ~3/1 by glc. The individual isomers [nmr of C*H*OR, τ 6.76 (m) cis; τ 7.01 (m) trans] were eventually separated by preparative glc using a 50-ft × 3/8-in. column, 30% FFAP on 50–60 Chromosorb W.

***cis*-2-Isopropylcyclopropanol and *trans*-2-Isopropylcyclopropanol.** The isomeric 2-chloroethyl 2-isopropylcyclopropyl ether mixture (15.0 g, 0.1 mol) reacted with *n*-butyllithium in hexane (Foote) to give 6.7 g (80%) of the isomeric alcohol mixture; bp 62–70° (35 mm); the cis/trans product ratio was *ca.* 3/1 by nmr. The pure cis alcohol [bp 64–66° (30 mm); nmr (neat) τ 5.0 (s, 1 H, CHOH), 6.57 (m, 1 H, C*H*OH), 8.98 (d, $J = 6$ Hz, 6 H, CH_3), 8.9–10.0 (m, 4 H)] and the pure trans alcohol [bp 64–65° (30 mm); nmr (neat) τ 4.97 (s, 1 H, O*H*), 7.03 (m, 1 H, C*H*OH), 8.6–10.1 (m, 4 H), 9.16 (d, $J = 6$ Hz, 6 H, CH_3)] were eventually prepared from the corresponding pure ether isomers.

***cis*-2-Isopropylcyclopropyl Tosylate (5b) and *trans*-2-Isopropylcyclopropyl Tosylate (5a).** 2-Isopropylcyclopropanol (3.0 g, 0.03 mol, mixture of isomers) and 6.1 g (0.032 mol) of tosyl chloride gave 4.8 g (65%) of the liquid **5**, cis/trans ratio *ca.* 3/1 by nmr.

Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.01; H, 7.06.

The individual liquid isomers **5a** [trans; nmr (neat) τ 2.43 (AB q, 4 H, C_6H_4), 6.29 (m, 1 H, C*H*OTs), 7.55 (s, 3 H, $C_6H_4CH_3$), 9.13 (d, 6 H, CH_3), 8.9–9.7 (m, 4)] and **5b** [cis; nmr (CCl_4) τ 2.43 (AB q, 4 H, C_6H_4), 6.01 (m, 1 H, C*H*OTs), 7.55 (s, 3 H, $C_6H_4CH_3$), 8.5–9.8 (m, 4), 9.03 (d, $J = 6$ Hz, 6 H, CH_3)] were eventually prepared from the isomerically pure alcohols.

2-Chloroethyl 2-*tert*-Butylcyclopropyl Ether. Dichloromethyl 2-chloroethyl ether[55] (40.0 g, 0.24 mol) was treated with specially prepared methyllithium[1] in the presence of an excess of 3,3-dimethyl-1-butene (Chemical Samples) to give 19.5 g (49%) of clear liquid product: bp 109–113° (50 mm); nmr (CCl_4) τ 6.44 (m, 4 H, OCH_2CH_2Cl), 6.88 (m, 1 H, C*H*OR), 9.02 (s, 3.7 H, *cis*-$C(CH_3)_3$), 9.17 (s, 5.3 H, *trans*-$C(CH_3)_3$), 9.5 (m, 3 H). The cis/trans isomer ratio was *ca.* 5/7 by nmr.

2-*tert*-Butylcyclopropanol. 2-Chloroethyl 2-*tert*-butylcyclopropyl ether (14.4 g, 0.107 mol, mixture of isomers) reacted with *n*-butyllithium in hexane (Foote) to give 6.2 g (53%) of clear liquid alcohol mixture: bp 66–73° (20 mm); nmr (CCl_4) τ 5.79 (s, 1 H, O*H*), 6.42 (m, 0.42 H, *cis*-C*H*OH), 6.84 (m, 0.58 H, *trans*-C*H*OH), 9.01 (s, 3.7 H, *cis*-$C(CH_3)_3$), 9.24 (s, 5.3 H, *trans*-$C(CH_3)_3$), 9.52 (m, 3 H). The cis/trans ratio was *ca.* 5/7 by nmr.

***cis*-2-*tert*-Butylcyclopropyl Tosylate (6b) and *trans*-2-*tert*-Butylcyclopropyl Tosylate (6a).** 2-*tert*-Butylcyclopropanol (4.6 g, 0.04 mol, mixture of isomers) and 15.3 g (0.08 mol) of tosyl chloride

(52) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 45–46.

(53) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 189.

(54) In a secondary cyclopropyl tosylate, the steric interaction is between the cis-β substituents and the oxygen bonded to C_α; the rest of the tosyl group can orient itself so as to avoid serious nonbonded interactions.

(55) H. Gross, A. Rieche, and E. Höft, *Chem. Ber.*, **94**, 544 (1961).

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

gave by the usual procedure[43] 9.5 g (89%) of liquid **6**: nmr (CCl_4) τ 2.51 (AB q, 4 H, C_6H_4), 6.2 (m. 1 H, C*H*OTs), 7.58 (s, 3 H, C_6H_4-CH_3), 9.08 (s, 5.3 H, *cis*-$C(CH_3)_3$), 9.28 (s, 3.7 H, *trans*-$C(CH_3)_3$). The cis/trans ratio was *ca.* 5/7 by nmr.

Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.70; H, 7.47; S, 11.95. Found: C, 62.43; H, 7.27; S, 12.20.

The pure cis isomer **6b** was prepared by preparative solvolysis in buffered acetic acid. Heating 5.2 g (0.02 mol) of **6** (isomeric mixture) at 100° for 2 hr gave 1.3 g (~60%) of white, crystalline **6b**: mp 30.5–31.0°; nmr (CCl_4) τ 2.51 (AB q, 4 H, C_6H_4), 6.14 (m, 1 H, C*H*OTs), 7.54 (s, 3 H, $C_6H_4CH_3$), 9.12 (s, 9 H, $C(CH_3)$), 9.47 (m, 3).

Bromocyclopropanes. Alkyl-substituted *gem*-dibromocyclopropanes[14,57] were prepared by the procedure described in detail below for 1,1-dibromo-2-*tert*-butylcyclopropane. Monobromocyclopropanes were obtained by reduction of the corresponding *gem*-dibromocyclopropanes with tri-*n*-butyltin hydride,[58] using the procedure of Seyferth, *et al.*[13]

1,1-Dibromo-2-*tert*-butylcyclopropane. 3,3-Dimethyl-1-butene (121 g, 1.25 mol, Chemical Samples Co.) and potassium *tert*-butoxide (78.4 g, 0.7 mol, K and K) were placed in a 1000-ml three-necked flask. Freshly distilled bromoform (202.5 g, 0.8 mol) was added dropwise at −10° under N_2 atmosphere. The mixture was stirred for 2 hr after addition was complete, then hydrolyzed with 200 ml of water. The organic layer was separated and the aqueous layer was extracted with two 50-ml portions of pentane. The combined organic solutions were dried over Na_2SO_4, stripped, and distilled to give 48.5 g (27%) of product: bp 81° (16 mm); nmr (CCl_4) τ 8.45 (m, 3 H), 8.92 (s, 9 H, $C(CH_3)_3$).

1-Bromo-*trans*-2-*tert*-butylcyclopropane (8a) and 1-Bromo-*cis*-2-*tert*-butylcyclopropane (8b). 1,1-Dibromo-2-*tert*-butylcyclopropane (24.4 g, 0.095 mol) was reduced with 27.7 g (0.095 mol) of tri-*n*-butyltin hydride to give 15.4 g (91%) of **8** in a trans/cis ratio of *ca.* 2 by nmr; bp 55° (25 mm).

Anal. Calcd for $C_7H_{13}Br$: C, 48.11; H, 7.34. Found: C, 48.16; H, 7.49.

The pure isomers **8a** [bp 82° (78 mm); nmr (CCl_4) τ 7.3 (d of t, 1 H, J_d = 7.0 Hz, J_t = 4.5 Hz, C*H*Br), 8.9 (m, 3 H), 9.13 (s, 9 H, $C(CH_3)_3$)] and **8b** [bp 80.5° (85 mm); nmr (CCl_4) τ 7.08 (d of t, 1 H, J_d = 5.5 Hz, J_t = 7.5 Hz, C*H*Br), 8.93 (s, 9 H, $C(CH_3)_3$), 9.1 (m, 3 H)] were separated by spinning band distillation.

1-Bromo-*trans*-2-methylcyclopropane (7a) and 1-Bromo-*cis*-2-methylcyclopropane (7b). 1,1-Dibromo-2-methylcyclopropane[57] (23.5 g, 0.11 mol) and tri-*n*-butyltin hydride (32.0 g, 0.11 mol) gave 8.2 g (61%) of **7** in a trans/cis ratio of *ca.* 1/2 by nmr; bp 95–104° (lit.[44] 85–94°).

Anal. Calcd for C_4H_7Br: C, 35.58; H, 5.23. Found: C, 35.65; H, 5.13.

The individual isomers **19a** [nmr (CCl_4) τ 7.50 (m, 1 H, C*H*Br), 8.80 (d, J = 5.5 Hz, 3 H, CH_3), 8.6–9.4 (m, 3 H)] and **19b** [nmr (CCl_4) τ 6.93 (m, 1 H, C*H*Br), 8.76 (d, 3, J = 6 Hz, CH_3), 8.6–9.7 (m, 3)] were obtained by preparative glpc on a 20 ft × 3/8 in. FFAP column (20% on 40–60 Chromosorb W) at 65°.

1-Bromo-*trans*-2,3-dimethylcyclopropane (10a) and 1-Bromo-*cis*,-*cis*-2,3-dimethylcyclopropane (10b). 1,1-Dibromo-*cis*-2,3-dimethylcyclopropane[14b,57] (25.1 g, 0.11 mol) and tri-*n*-butyltin hydride (32.0 g, 0.11 mol) gave 11.0 g (67%) of **10**, bp 52–53° (60 mm) [lit.[57] 51° (58 mm)]. The cis/trans product ratio was *ca.* 14/3 by nmr [(CCl_4) τ 6.86 (m, 0.82 H, *cis*-C*H*Br), 7.85 (m, 18 H, *trans*-C*H*Br), 9.00 (m, 8)]. The solvolysis rates of **8a** and **8b** were determined by using the mixture of isomers.

Anal. Calcd for C_5H_9Br: C, 40.29; H, 6.09. Found: C, 40.17; H, 5.99.

1-Bromo-*cis*,*trans*-2,-dimethylcyclopropane (12). 1,1-Dibromo-*trans*-2,3-dimethylcyclopropane[14b,57] (22.8 g, 0.1 mol) and 29.1 g (0.1 mol) of tri-*n*-butyltin hydride gave 6.9 g (46%) of **12**: bp 45° (22 mm) (lit.[57] 111°); nmr (CCl_4) τ 7.37 (m, 1, H, C*H*Br), 8.88 (m, 6 H, CH_3), 9.28 (m, 2 H).

Anal. Calcd for C_5H_9Br: C, 40.29; H, 6.09. Found: C, 40.40; H, 6.02.

1-Bromo-*trans*-2,2,3-trimethylcyclopropane (14a) and 1-Bromo-*cis*-2,2,3-trimethylcyclopropane (14b). 1,1-Dibromo-2,2,3-trimethylcyclopropane[14b,57] (30.0 g, 0.124 mol) and tri-*n*-butyltin hydride (36.0 g, 0.124 mol) gave 13.2 g (65%) of **14**, bp 61–63° (68 mm), with the trans/cis product ratio *ca.* 3/7 by nmr. The pure isomers, colorless oils, **14a** [nmr (CCl_4) τ 7.60 (d, 1 H, J = 6 Hz, C*H*Br), 8.8–9.5 (m, 10)] and **14b** [nmr (CCl_4) τ 7.06 (d, 1 H, J = 12 Hz), 8.8–9.5 (m, 10 H)] were separated by preparative glpc using an FFAP column at 135°.

Anal. Calcd for $C_6H_{11}Br$: C, 44.19; H, 6.80. Found (**12a**): C, 44.11; H, 6.90. Found (**12b**): C, 43.97; H, 6.96.

1-Bromo-2,2,3,3-tetramethylcyclopropane (16). 1,1-Dibromo-2,2,3,3-tetrabromocyclopropane[14b] (20.0 g, 0.078 mol) and tri-*n*-butyltin hydride (22.8 g, 0.078 mol) gave 8.1 g (59%) of **16**: bp 69° (54 mm) (lit.[13] 51° (22 mm)); nmr (CCl_4) τ 7.35 (s, 1 H, C*H*Br), 8.85 (s, 6 H, *cis*-CH_3), 8.91 (s, 6 H, *trans*-CH_3).

Anal. Calcd for $C_7H_{13}Br$: C, 48.11; H, 7.34. Found: C, 48.23; H, 7.12.

Chlorocyclopropanes. The 1-chloro-2,3-dimethylcyclopropanes (**11** and **13**) and 1-chloro-2,2,3-trimethylcyclopropane (**15**) were synthesized as described by Closs and Closs.[15] The individual isomers **11a** [bp 96° (atm); nmr (CCl_4) τ 7.71 (t, 1 H, J = 3 Hz, C*H*-Cl), 8.9 (s, 6 H, CH_3), 8.95 (m, 2)] and **11b** [bp 104° (atm); nmr (CCl_4) τ 6.81 (t, 1 H, J = 7.5 Hz, C*H*Cl), 8.97 (m, 8 H)] were separated by spinning band distillation. The isomeric ratio (**15a**/**15b**) was *ca.* 5/8 by nmr [(CHCl) cis (**15b**), τ 7.21 (d, J = 7 Hz); trans (**15a**), 7.60 (d, J = 3.5 Hz)]. Rate constants for **15a** and **15b** were determined by using the mixture of isomers.

1-Chloro-*trans*-2-*tert*-butylcyclopropane (9a) and 1-Chloro-*cis*-2-*tert*-butylcyclopropane (9b). The method of Closs and Closs[15] was employed. Working at 0–10°, 124 g (1.48 mol) of 3,3-dimethylbutene (Aldrich), 250 g (2.95 mol) of dichloromethane, and 265 ml of methyllithium (Foote, 1.67 *N* in diethyl ether) gave *ca.* 2 g of crude **9** as a dark oil. The crude **9** (trans/cis ratio about 3/2 by nmr) was not distilled, but the individual isomers **9a** [nmr (neat) τ 7.19 (d of t, 1 H, J_d = 7.0 Hz, J_t = 4.5 Hz, C*H*Cl), 9.19 (s, 9 H, $C(CH_3)_3$), 8.8–9.4 (m, 3 H)] and **9b** (nmr (neat) τ 6.98 (d of t, 1 H, J_d = 4.5 Hz, J_t = 6.5 Hz, C*H*Cl), 8.98 (s, 9 H, $C(CH_3)_3$, 9.05–9.35 (m, 3 H)] were separated by preparative glpc using a 20 ft × 3/8 in. SE-30 column (20% on 50–60 Chromosorb P).

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.49. Found (cis (**9b**): C, 64.48; H, 8.42. Found (trans (**9a**): C, 64.61; H, 8.50.

Kinetic Studies. All kinetics were carried out titrimetrically using the sealed ampoule technique as described in the preceding paper,[1] with Volhard titrations[16] being used to follow all cyclopropyl halide acetolyses.

Acknowledgments. We wish to thank Professor U. Schöllkopf for the stimulus he has provided for our work in this area. Support from the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-LaRoche, Nutley, N. J., is gratefully acknowledged.

(57) J. M. Harris, Ph.D. Thesis, The University of Texas at Austin, 1969.

(58) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 7, 366 (1957).