Cyclopropylcarbinyl Pentamethylbenzenesulfonate Solvolysis. A Study of Response to Solvent Ionizing Strength

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Received March 13, 1979

The solvolysis rates of cyclopropylcarbinyl pentamethylbenzenesulfonate (**3-OPms**) have been determined in a series of aqueous alcohol and carboxylic acid solvents. The kinetic data indicate that **3-OPms** ionizes via the k_Δ pathway and that neighboring-group assistance by the cyclopropane ring is characterized by a different response to solvent ionizing strength than that by an aryl group.

The unusual solvolytic behavior of cyclopropylcarbinyl derivatives has long been known.[1] It is now apparent that neighboring-group participation in both the rate-controlling and product-determining steps occurs via σ-bond delocalization of charge into the cyclopropane ring.[1,2] More recently,[3] it has been demonstrated that the extent of the nuclear reorganization accompanying this σ-bond delocalization can vary from little or no rearrangement (hyperconjugative interactions) to complete formation of a fully delocalized three-center, two-electron bond (σ bridging).

Considerable evidence[4] has also been collected to support the contention that the σ-bond delocalization of charge in the cyclopropylcarbinyl cation formed in the rate-controlling step differs from that in the carbocationic intermediate(s) eventually captured by solvent. In Scheme I we have represented the rate-controlling step in the solvolysis of cyclopropylcarbinyl arenesulfonates as an ionization to a tight ion pair, assisted by hyperconjugative stabilization. Subsequent reorganization affords the carbocationic species responsible for the observed product distribution,[4a,5] generally interpreted in terms of a rapidly equilibrating bicyclobutonium ion system,[6,7] which is common to solvolysis of cyclopropylcarbinyl, cyclobutyl, and allycarbinyl substrates.

Scheme I

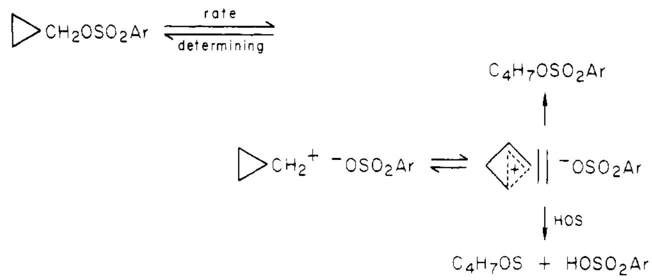

Table I. Summary of Solvolysis Rates for Cyclopropylcarbinyl Pentamethylbenzenesulfonate

solvent[a]	T, °C	$10^{-4}k_t$, s^{-1}	infinity,[b] %	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
EtOH	25	0.08	93	22.9	−5.3
	30	0.15	93		
	40	0.55	93		
	50	1.70	92		
90% EtOH	30	1.22			
	40	3.70	96		
80% EtOH	30	4.5	96		
	40	13	96		
TFE	15	5.2	68		
	25	15.6			
AcOH	25	0.33	50	21.7	+1.7
	30	0.60	48		
	40	1.83	48		
	47	4.5	50		
	50	6.0	48		
HCO_2H	5	74	67	15.2	−13.4
	10	128	67		
	15	183	67		

[a] TFE = 2,2,2-trifluoroethanol. [b] Millimoles of acid titrated at 10 or more half-lives divided by millimoles of ester at zero reaction time.

The mY equation of Winstein and Grunwald[8] has become a very useful tool for evaluating the mechanism of a solvolysis reaction. It is now common, for example, to assess sensitivity to solvent ionizing power and nucleophilicity in terms of four standard criteria derived from the mY equation. They are m_{EW}, the slope of the aqueous ethanol correlation line, and m_{AF}, the slope for acetic and formic acids, $[k_{EW}/k_{AcOH}]_Y$ and $[k_{EW}/k_{HCO_2H}]_Y$, the ratio of rates in two solvents of equal Y but different nucleophilicity. Collection of these solvent parameters, however, for cyclopropylcarbinyl arenesulfonates (**3**) has proven to be difficult.[10] In solvents with Y values greater than that of 75% AcOH–HCOOH, the solvolytic reactivity of **3** is too high for accurate measurement of k_t, the titrimetric rate constant.

Recently,[11] pentamethylbenzenesulfonates (OPms) have been reported to be some 8.5 times less reactive than tosylates. Such a retardation of the solvolytic reactivity

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[1] (a) For a review, see chapters by H. G. Richey, Jr., and by K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Eds., Vol. III, Wiley-Interscience, New York, N.Y., 1972. (b) For leading references, see P. v. R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

[2] (a) D. D. Roberts, *J. Org. Chem.*, **35**, 4059 (1970); (b) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 302 (1974). (c) For a detailed discussion, see: W. J. Hehre, *Acc. Chem. Res.*, **8**, 369, (1975); (d) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975).

[3] (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970); (b) G. A. Olah and G. Liang, *ibid.*, **97**, 6803 (1975); (c) G. A. Olah, R. J. Spear, P. C. Hiberty, and W. J. Hehre, *ibid.*, **98**, 7470 (1976).

[4] (a) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964); (b) D. D. Roberts, *ibid.*, **30**, 23 (1965); (c) D. D. Roberts, *ibid.*, **31**, 2000 (1966); (d) D. D. Roberts, *ibid.*, **33**, 2712 (1968); (e) D. D. Roberts, *ibid.*, **34**, 285 (1969); (f) D. D. Roberts and T. M. Watson, *ibid.*, **35**, 978 (1970).

[5] (a) D. D. Roberts, *J. Org. Chem.*, **35**, 4059 (1970); (b) D. D. Roberts, *ibid.*, **36**, 1913 (1971).

[6] (a) K. J. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964); (b) G. A. Olah, C. L. Jewell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972); (c) D. D. Roberts, *J. Org. Chem.*, **37**, 1510 (1972).

[7] For a recent review, see T. H. Lowery and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, N.Y., 1976, pp 293–300.

[8] (a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); (c) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, pp 45–47, 63–65.

[9] T. W. Bentley and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7658 (1976)

[10] The estimated k_t value for formolysis of cyclopropylcarbinyl tosylate is 1.9×10^{-1} s^{-1}.

[11] C. M. Paleos, F. S. Varveri, and G. A. Gregoriou, *J. Org. Chem.*, **39**, 3594 (1974).

0022-3263/79/1944-2860$01.00/0

Table II. Summary of Solvent Parameters Derived from the mY Equation

substrate	m_{EW}	m_{AF}	$[k_{EW}/k_{AcOH}]_Y$	$[k_{EW}/k_{HCO_2H}]_Y$
p-MeO-neophyl-OTs[a-c]	0.42	0.59	0.50	0.10
neophyl-OTs[d,e]	0.39	0.59	0.37	0.07
neopentyl-OTs[a,f]		0.74		
cyclopropylcarbinyl-OTs[g,h]	0.74		0.49	
cyclopropylcarbinyl-OPms[a,i]	0.76	0.84	0.48	0.23
exo-2-norbornyl-OTs[j]	0.81	0.90	0.50	0.20

[a] 25 °C. [b] Reference 9. [c] Reference 15. [d] Reference 12a. [e] 75 °C. [f] Calculated from data reported in ref 16a. [g] Calculated from data reported in ref 4f. [h] 20 °C. [i] Calculated from data listed in Table I. [j] J. M. Harris, D. L. Mount, and D. J. Raber, *J. Am. Chem. Soc.*, **100**, 3139 (1978).

of **3** is sufficient to extend to formic acid the range of solvents in which k_t can be measured. Thus, in this paper we report the kinetic investigation of the solvolytic reactions of cyclopropylcarbinyl pentamethylbenzenesulfonate (**3-OPms**) in a series of solvents ranging from ethanol to formic acid.

The data indicate that **3-OPms** ionizes via the k_Δ pathway[12] and that neighboring-group assistance by the cyclopropane ring is characterized by a different response to solvent ionizing strength than that by an aryl group.

The first-order rate constants for solvolysis of **3-OPms** in the usual series of solvents, ranging from ethanol to formic acid, are collected in Table I. The course of reaction was followed by titrating the liberated pentamethylbenzenesulfonic acid. The solvolysis reactions in all solvents were accompanied by internal-return isomerization,[4b,13] and consequently the apparent first-order rate constants, k_t, were computed on the basis of the acid-infinity titer.[14]

Values of m_{EW}, m_{AF}, $[k_{EW}/k_{AcOH}]_Y$, and $[k_{EW}/k_{HCO_2H}]_Y$ for solvolysis of various arenesulfonates are collected in Table II. Neophyl and *p*-methoxyneophyl tosylates are thought to solvolyze by aryl participation and internal return.[12a,15] Neopentyl tosylate is thought to solvolyze by alkyl participation without nucleophilic solvent participation and internal return,[16a] while *exo*-2-norbornyl tosylate is thought to solvolyze with anchimeric assistance and without nucleophilic solvent participation.[17,18]

The data collected in Table II show that the *m* values for **3-OPms** are slightly higher than those listed for other primary substrates solvolyzing by the k_Δ pathway. This higher than usual sensitivity to solvent ionizing power is in line with the high *b* value reported[19] for the acetolysis of cyclopropylcarbinyl β-naphthalenesulfonate. The $[k_{EW}/k_{AcOH}]_Y$ and $[k_{EW}/k_{HCO_2H}]_Y$ values for **3-OPms** are within the range proposed by Schleyer[9] for solvolysis of arenesulfonates occurring without nucleophilic solvent assistance and internal return.

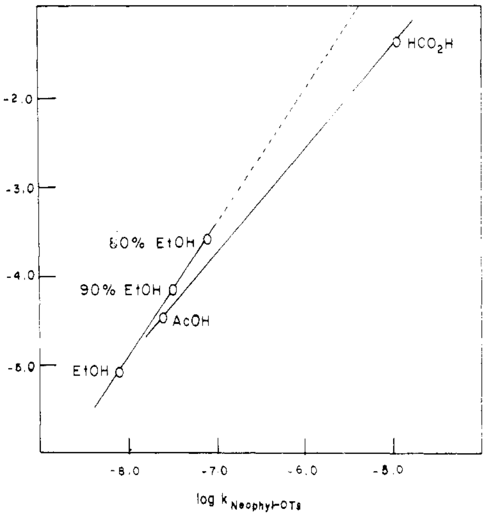

Figure 1. Plot of log k_t(**3-OPms**) against log k_t(neophyl-OTs) in various solvents at 25 °C. Data taken from Table III.

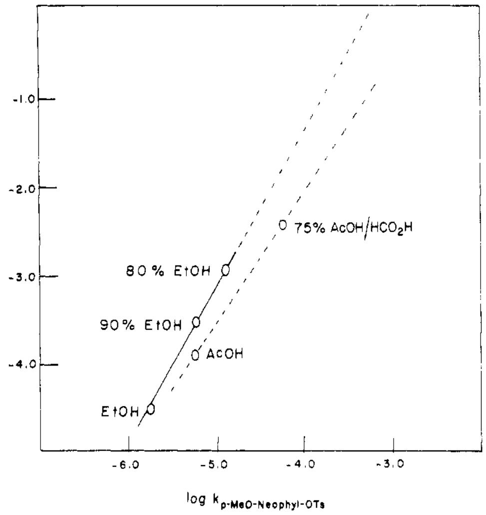

Figure 2. Plot of log k_t(**3-OTs**) against log k_t(*p*-MeO-neophyl-OTs) in various solvents at 20 and 25 °C, respectively. Data taken from Table III.

When log k_t values for **3-OPms** are plotted against log k_t(neophyl-OTs) in various solvents, a dispersion is observed (see Figure 1), and lines of different slopes are observed for ethanol/water on the one hand and the carboxylic acids formic and acetic on the other. This result stands in sharp contrast to the quantitative correlations reported by Winstein for 2-phenyl-1-ethyl tosylate and related systems.[12a,21]

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(12) (a) A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968); (b) J. L. Coke, F. E. McFarlane, M. C. Mouring, and M. G. Jones, *ibid.*, **91**, 1154 (1969); (c) S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *ibid.*, **91**, 4571 (1969).

(13) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(14) (a) K. L. Servis and J. D. Roberts, *Tetrahedron Lett.*, 1369 (1967); (b) R. S. Macomber, *J. Org. Chem.*, **36**, 2182 (1971).

(15) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(16) (a) J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, **88**, 4475 (1966); (b) J. L. Frey, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

(17) See comments by P. v. R. Schleyer to Chapter 8 in H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977.

(18) G. D. Sargent in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, p 1099.

(19) D. D. Roberts, *J. Org. Chem.*, **35**, 4059 (1970).

(20) The log k_t value for the formolysis of **3-OTs** is, of necessity, an estimated value.[10] It was calculated from a k_{OTs}/k_{OPms} ratio of 6.7. This is the rate ratio found for the acetolysis of **3-OTs** and **3-OPms** at 20 °C. Inclusion of the solvolysis data for ethanol/water increases the k_{OTs}/k_{OPms} ratio only slightly.

(21) (a) I. L. Reich, A. F. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969); (b) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

Table III. Solvolysis Rates (-log k_t)[a] for Selected Substrates in Various Solvents[b] at 25 °C

substrate	100E	90E	80E	AcOH	75AcOH-HCOOH	HCOOH
3-OPms	5.10	4.15	3.60	4.48		1.37
3-OTs[c]	4.49[d]	3.50[e]	2.94[d]	3.89[d]	2.54[d,f]	
neophyl-OTs	8.12[g]	7.47[h]	7.10[i]	7.60[j]		4.94[k]
p-MeO-neophyl-OTs	5.75[l]	5.20[m]	4.85[l]	5.27[l]	4.26[l]	3.08[l]
exo-2-norbornyl-OTs	5.35[n]	4.15[o]	3.64[o]	4.63[p]		1.29[q]

[a] In s^{-1}. [b] E = aqueous ethanol. Numbers are percent by volume of ethanol and acetic acid, respectively. [c] At 20 °C. [d] Reference 4a. [e] Reference 4f. [f] D. D. Roberts, unpublished result. [g] Calculated from data at higher temperatures contained in ref 12a and 15. [h] Obtained from a plot of log *k*(neophyl-OTs) vs. *Y* for aqueous alcohol solvents. [i] Calculated from data at higher temperatures contained in ref 15 and 25. [j] B. K. Morse, E. Grunwald, K. C. Schreiber, J. Corse, and S. Winstein, *J. Am. Chem. Soc.*, **74, 1113 (1952)**. [k] Reference 12a. [l] Reference 15. [m] Obtained from a plot of log *k*(*p*-MeO-neophyl-OTs) vs. *Y* for aqueous alcohol solvents. [n] W. Huckel and O. Vought, *Chem.*, **695**, 16 (1966). [o] J. M. Harris, D. L. Mount, and D. J. Raber, *J. Am. Chem. Soc.*, **100**, 3139 (1978). [p] P. V. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965). [q] H. C. Brown and I. Rothberg, unpublished results.

Possible explanations for this unusual result include (1) differences in leaving-group solvation, (2) the presence of an ion-return effect in the solvolysis of **3-OPms**, and (3) a characteristically different response to solvent effect by a substrate ionizing with assistance by σ–π conjugation from one ionizing with neighboring-group participation (essentially internal displacement).

If the dispersion observed in Figure 1 is due to differences in leaving-group solvation, then changing the leaving group of the cyclopropylcarbinyl substrate from pentamethylbenzenesulfonate to tosylate should eliminate the dispersion of solvolysis rate data. However, a plot of log k_t values for **3-OTs** against log k_t(neophyl-OTs) in the solvents listed in Table I (see Figure 2) reveals no such single linear correlation. Rather the data for **3-OTs** yield a plot which appears[20] to be quite similar to that of **3-OPms**. Explanation 2 is also considered unlikely. While we have no direct evidence regarding the extent of internal return in the cyclopropylcarbinyl system,[22] it can be deduced,[9] nevertheless, from the low values of $[k_{EW}/k_{AcOH}]_Y$ that internal ion-pair return is not significant in this system in acetic acid, formic acid, and ethanol/water.

Having eliminated the first two proposals from consideration as possible explanations for the dispersion observed in Figure 1, we are led to proposal 3. As a test of this proposal, we have plotted the log k_t values for **3-OPms** against log k_t(*exo*-2-norbornyl-OTs)—another strained system where σ–π conjugation might provide significant stabilization to the transition state for a σ-bond-assisted reaction. As can be seen from Figure 3, the rate data for the two compounds are correlated by a single straight line. Accordingly, we conclude that the dispersion observed in Figure 1 can be attributed to the unique properties of the cyclopropylcarbinyl system caused by conjugative interaction between a strained bonding orbital and an adjacent cation center. We also propose that plots of log k_t against log k_t(neophyl-OTs) might well be a useful tool for distinguishing between σ-bond stabilization of neighboring cation centers by σ–π conjugation and σ-bond stabilization of such centers by internal displacement.

Experimental Section

Pentamethylbenzenesulfonyl chloride was prepared several times according to the method of Gregoriou et al.[11] In a typical run, a 0.75 M solution of chlorosulfonic acid in dry chloroform (70 g of $ClSO_3H$ in 800 mL of $CHCl_3$) was added dropwise over a period of about 90 min to a stirred 0.25 M solution of pentamethylbenzene in dry chloroform (29.6 g of pentamethylbenzene in 800 mL of $CHCl_3$) kept at about -5 °C during the addition. The reaction mixture was allowed, with continued stirring, to reach room temperature over a 2-h period. Then it was allowed to stand at room temperature, without stirring, for 72 h. The resultant reaction mixture was poured into 5% aqueous sodium carbonate containing crushed ice. The chloroform layer was washed with cold 5% aqueous sodium bicarbonate followed by saturated aqueous sodium chloride and was dried over magnesium sulfate. The solvent was removed by rotovaporization. The solid residue was recrystallized from petroleum ether (bp 30–60 °C) to give 37 g (75%) of the purified product; mp 79–80 °C (lit.[11] mp 80–81 °C).

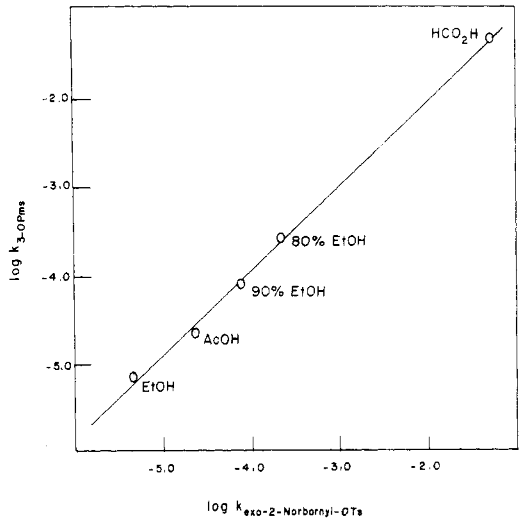

Figure 3. Plot of log k_t(**3-OPms**) against log k_t(*exo*-2-norbornyl-OTs) in various solvents at 25 °C. Data taken from Table III.

Cyclopropylcarbinyl Pentamethylbenzenesulfonate (3-OPms). To a hand-stirred solution of cyclopropylcarbinol (2.0 g, 28 mmol, Aldrich Chemical Co.) in 40 mL of dry pyridine (spectrophotometric grade, Aldrich Chemical Co.) cooled to 0 °C was added all at once 7.4 g (30 mmol) of purified pentamethylbenzenesulfonyl chloride. After standing 24 h at about 4 °C, the mixture was carefully hydrolyzed by the slow addition of 20 mL of ice (reaction temperature maintained between 0 and 5 °C) followed by the addition of sufficient cold, dilute HCl to acidify the mixture (reaction temperature maintained between 5 and 10 °C). The precipitated ester was separated on a Büchner funnel and washed several times with cold, dilute HCl, several times with cold water, and then once with cold petroleum ether (bp 30–60 °C) and after air-drying yielded 6.0 g (76%) of white powder. Recrystallization from petroleum ether (bp 30–60 °C)-benzene (4:1) gave 4.7 g (59%) of white crystals; mp 80–81 °C. Anal. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.185; S, 11.35. Found: C, 63.87; H, 7.77; S, 11.19.

Solvents. Acetic acid solvent was prepared from 994.9 mL of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 mL

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[22] Detection of this phenomenon is complicated by the possible internal return, without rearrangement, from the bicyclobutonium-arenesulfonate ion pair.[5b]

of acetic anhydride. Formic acid solvent was prepared by storing practical grade formic acid (Eastman Kodak Co., 97%) over boric anhydride for several days, decanting, and distilling from fresh anhydride. Absolute ethanol was prepared according to the method of Fieser.[23] 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled just prior to use.

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions in formic acid were 0.02 M. In all other solvents the solutions were 0.03 M. In a typical kinetic run, the requisite amount of ester was accurately weighed into a 25-mL volumetric flask and then sufficient solvent was added rapidly to give a 25-mL reaction solution volume. Reaction time commenced with the addition of the solvent.[24] The solvent used for each kinetic run and the flask containing the ester were thermostated in a constant-temperature bath held to ±0.05 °C at least 20 min prior to a run. At appropriate times, 2-mL aliquots were analyzed for liberated pentamethylbenzenesulfonic acid. In acetic acid and ethanol, aliquots were titrated directly. The aliquots taken from the trifluoroethanol and aqueous ethanol solvents were quenched with 5-mL of cold ethanol before titration, while those taken from formic acid were quenched with 8 mL of cold, purified dioxane[26] before titration. The titrating solutions were for acetolysis and formolysis 0.050 N sodium acetate in acetic acid and for the alcoholyses 0.020 N sodium methoxide in anhydrous methanol. The indicators used were the following: for acetolysis, bromophenol blue (in acetic acid); for formolysis, bromocresol green (in acetic acid); for trifluoroethanolysis, bromophenol blue (in 20% aqueous EtOH); for alcoholyses, bromothymol blue (in water).

Registry No. 3-OPms, 70561-86-3; cyclopropylcarbinol, 2516-33-8; pentamethylbenzenesulfonyl chloride, 52499-94-2.

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(23) L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed., D. C. Heath, Boston, Mass., 1957, p 285.

(24) The ester dissolved rapidly—within a few seconds— in all solvents except formic acid. To effect rapid dissolution in this solvent, the ester was fluidized with 15 drops of ethyl acetate before addition of the formic acid. As measured in our laboratory,[25] this quantity of ethyl acetate has no effect on the observed rate of such formolysis reactions.

(25) D. D. Roberts, unpublished data.

(26) Purified by percolation through chromatographic grade alumina (Aluminum Co. of America, F-20 grade).

Conformational Preference of the Sulfimide Functionality in Cyclic Sulfimides

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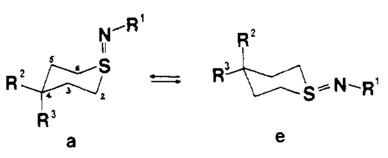
Received April 4, 1979

Conformational equilibria of various >S=N—R derivatives (R = C_6H_4X, SO_2Ar, COAr, COOEt, COMe) of thiane and of some oxa- and dithianes were determined by low-temperature ^{13}C NMR spectroscopy. The conformational preference of the thiane 1-(*N*-aryl)imides was found to depend on the electron-withdrawing capacity of the substituents on the aromatic ring. Replacement of the aromatic ortho hydrogens by methyl or fluorine did not greatly change the equilibrium. A nearly constant difference in conformational free energy was found between 1-[*N*-(*p*-chlorophenyl)]imides and 1-oxides for the various heterocyclic ring systems investigated.

Recently we reported a pronounced preference of the S=N bond in thiane 1-[*N*-(*p*-chlorophenyl)]imide (**1**) for the equatorial conformation,[1] in contrast to the *N*-H (**2**),[2] the *N*-benzoyl (**3**),[3] and the *N*-tosyl (**4**)[2,3] analogues and to the S=O bond in thiane 1-oxide.[2,4] In 1,3-dithiane 1-*N*-imides only the N-equatorial form could be observed[3,5] at low temperature, regardless of the substituent on nitrogen, similar to the situation in 1,3-dithiane 1-oxide.[6]

Scheme I



1, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = R^3 = H$
2, $R^1 = R^2 = R^3 = H$
3, $R^1 = COC_6H_5$, $R^2 = R^3 = H$
4, $R^1 = SO_2C_6H_4CH_3$, $R^2 = R^3 = H$
5, $R^1 = COOC_2H_5$, $R^2 = R^3 = H$
6, $R^1 = COCH_3$, $R^2 = R^3 = H$
7, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = CH_3$, $R^3 = H$
8, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = H$, $R^3 = CH_3$
9, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = R^3 = CH_3$
10, $R^1 = COC_6H_5$, $R^2 = R^3 = CH_3$
11, $R^1 = SO_2C_6H_4CH_3$, $R^2 = R^3 = CH_3$
12, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = Cl$, $R^3 = H$
13, $R^1 = p\text{-}C_6H_4Cl$, $R^2 = H$, $R^3 = Cl$

In an attempt to explain the preference for the axial position of oxygen in thiane 1-oxides, Johnson[7] originally suggested that attractive London interactions might outweigh van der Waals repulsions. This was subsequently confirmed in Westheimer-type calculations by Allinger[8] and has been used to explain the conformational equilibria

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(1) P. K. Claus, W. Rieder, F. W. Vierhapper, and R. L. Willer, *Tetrahedron Lett.*, 119 (1976).

(2) (a) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, 31, 3429 (1966); (b) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Am. Chem. Soc.*, 94, 208 (1972); (c) J. B. Lambert, C. E. Mixan, and D. H. Johnson, *ibid.*, 95, 4634 (1973); (d) J. B. Lambert and S. I. Featherman, *Chem. Rev.*, 75, 611 (1975).

(3) P. K. Claus, F. W. Vierhapper, and R. L. Willer, *J. Chem. Soc., Chem. Commun.*, 1002 (1976).

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