Cyclopropylcarbinyl p-Toluenesulfonate Solvolysis. 1-Ring Substituent Effect

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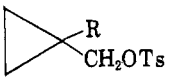
Solvolysis rates of the p-toluenesulfonate derivative of ethanol, benzyl alcohol, cyclopropylcarbinol (Ia), and 1-phenylcyclopropylcarbinol (Ib) have been determined in a series of solvents of varying nucleophilic strength. The relative rates as well as the product distribution of Ia are dependent on the nucleophilic strength of the solvent. Application of an isokinetic treatment indicates variable substrate contribution to Ia activation parameters in distinct contrast to near invariant substrate contribution to Ib activation parameters. Assessment of driving force for neighboring group assistance reveals a correlation between Ib transition-state geometry and corresponding benzyl cation.

In the previous paper[1] in this study, the apparent insensitivity of the acetolysis rate of cyclopropylcarbinyl p-toluenesulfonate to 1-ring substituents was dis-



Ia, R = H
b, R = C_6H_5
c, R = CH_3

cussed in terms of both variable transition state geometry as evidenced by the influence of R on the solvolysis products and transition state solvation effects as evidenced by differences in the partitioning of the activation parameters and sensitivity to solvent ionizing strength.

Further consideration of the failure of the structural change in I to affect the reaction rate led to the question of whether the reaction mechanism involves any variable interactions between the reaction site and the 1-ring position. A well-established technique frequently used to measure such interactions is the study of the effect of variable solvation forces on the activation parameters. It was, therefore, thought of interest to extend the earlier investigation to include a wider range of solvation forces.

In the present paper, solvolysis rate measurements, activation parameters, and solvolysis products (in part) have been obtained for the p-toluenesulfonate esters of cyclopropylcarbinol, 1-phenylcyclopropylcarbinol, ethanol, and benzyl alcohol in five additional solvent systems. These data not only corroborate the earlier findings but provide additional insight relative to 1-ring substituent effects on the cyclopropylcarbinyl system.

Results

The kinetic data are summarized in Table I. Each of these esters was allowed to solvolyze in the indicated solvent and the course of reaction was followed by titrating the liberated p-toluenesulfonic acid. The solvolysis reactions of cyclopropylcarbinyl tosylate in 90% acetone and sulfolane demonstrated the previously reported "internal return" rearrangement[2] which accounted for about 15% of the starting material. The purities of the starting materials were, therefore, checked by ethanolysis where a rearrangement to less reactive arenesulfonates does not occur.[3] The solvolysis rates in 90% acetone and sulfolane were calculated by a graphical technique from the initial slope of the rate curves.[1,4]

All other reactions were strictly first order in p-toluenesulfonate and furnished, within experimental error, 100% of the theoretical amount of acid present.

Table II compares the relative rates of the four tosylates in six solvents. It is clear that the replacement of the 1-ring hydrogen by phenyl has remarkedly little influence on the rate of reaction. It is also apparent that the enhanced reactivity of Ia and Ib is diminished by increased solvent nucleophilicity (compare reactivity in sulfolane to reactivity in DMSO). The fact, however, that both Ia and Ib exhibit a greater sensitivity to solvent ionizing strength[1] than p-methoxyneophyl tosylate, a primary ester found to follow the SN1 mechanism in a large variety of solvents,[5] militates against any mechanism other than SN1 for these esters.

The selection of the solvents was suggested by the previously observed[1] solvolytic behavior of cyclopropylcarbinyl tosylate; *i.e.*, solvents of high ionizing power promote complex kinetics and a mixture of products whereas nucleophilic solvents promote simple kinetics and a single product. The data reported in Table III lend further support to this postulate. It is interesting to note that the solvolytic behavior of 1-phenylcyclopropylcarbinyl tosylate in all the solvents with the exception of ethanol reveals the strong influence of the 1-phenyl substituent on the reaction products.

Extrathermodynamic Analysis of Enthalpy and Entropy Changes.—Comparison of the two thermodynamic quantities for a single reaction series has proven to be a valuable tool for assessing the number of interaction mechanisms associated with a particular variable. Thus, Leffler[6] derived the following isokinetic relationship which has been successfully applied to a

$$\Delta H^* = \beta\Delta S^* + \Delta H_0^* \quad (1)$$

variety of structure and solvent effects. Since relation 1 is sensitive to abrupt changes in solvation interaction mechanisms,[6,7] it is instructive to analyze the activation parameters reported in Table I by a plot of ΔH^* *vs.* ΔS^*.

The poor correlation for cyclopropylcarbinyl tosylate (*cf.* Figure 1, correlation coefficient = 0.94, $\beta = 230°$) is in distinct contrast with the good correlation obtained for 1-phenylcyclopropylcarbinyl tosylate. (*cf.* Figure 2,

(1) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).
(2) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).
(3) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).
(4) S. Borcic, M. Nikoletic, and D. E. Sunko, *ibid.*, **84**, 1615 (1962).
(5) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).
(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.
(7) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 863 (1956).

TABLE I

SUMMARY OF SOLVOLYSIS RATES FOR ORGANIC TOSYLATES

Solvent	Concn., 10^2 M	Temp., °C.	k_1,[a] 10^5 sec.$^{-1}$	ΔH^*,[b] kcal.	ΔS^*,[b] e.u.
			Cyclopropylcarbinyl tosylate (Ia)		
90% acetone	3.70	25.0	4.67 ± 0.15	17.0 ± 0.60	−21.5 ± 2.0
	3.70	30.0	7.67 ± 0.20		
	3.70	40.0	20.0 ± 0.20		
	3.70	50.0	46.0 ± 0.25		
Sulfolane[c]	3.75	35.0	1.07 ± 0.15	15.8 ± 0.60	−30.0 ± 2.0
	3.75	40.0	1.67 ± 0.17		
	3.45	50.0	4.4 ± 0.25		
	3.45	60.0	8.0 ± 0.30		
CH_3OH	3.62	10.0	3.80 ± 0.20	20.1 ± 0.34	−7.3 ± 1.0
	3.80	20.0	13.50 ± 0.20		
	3.62	25.0	25.0 ± 0.40		
	3.70	30.0	43.0 ± 1.8		
DMSO[d]	2.60	20.0	7.2 ± 0.20	16.9 ± 0.20	−20.0 ± 1.0
	2.60	30.0	19.7 ± 0.50		
	2.60	35.0	31.7 ± 1.2		
	2.60	40.0	48.7 ± 0.70		
i-PrOH	2.75	25.0	3.7 ± 0.10	16.3 ± 0.40	−24.2 ± 1.5
	2.62	30.0	5.7 ± 0.30		
	2.62	40.0	15.3 ± 0.20		
	2.80	50.0	32.5 ± 1.0		
			1-Phenylcyclopropylcarbinyl tosylate (Ib)		
90% acetone	3.00	25.0	3.50 ± 0.01	19.0 ± 0.20	−15.3 ± 1.0
	3.00	30.0	5.8 ± 0.10		
	3.00	50.0	45.0 ± 0.40		
Sulfolane[c]	3.00	30.0	5.7 ± 0.25	17.0 ± 0.30	−22.0 ± 1.0
	3.00	40.0	14.7 ± 0.60		
	3.00	50.0	34.2 ± 0.70		
CH_3OH	3.00	10.0	4.00 ± 0.05	20.4 ± 0.28	−6.6 ± 1.0
	3.00	20.0	14.2 ± 0.30		
	3.00	25.0	25.7 ± 0.30		
	3.00	30.0	45.0 ± 0.60		
DMSO[d]	2.00	20.0	7.83 ± 0.20	18.0 ± 0.45	−16.0 ± 1.6
	2.00	30.0	22.5 ± 0.30		
	2.00	35.0	36.5 ± 0.60		
	2.00	40.0	58.5 ± 0.80		
			Ethyl tosylate		
90% acetone	4.00	55.0	0.084 ± 0.008	19.9 ± 0.50	−27.9 ± 1.5
	4.00	45.0	0.031 ± 0.001		
	4.00	35.0	0.010 ± 0.0003		
Sulfolane[c]	4.00	55.0	0.0007 ± 0.00003		
	4.00	100.0	0.017 ± 0.0004		
DMSO[d]	4.00	30.0	0.30 ± 0.01	19.6 ± 0.40	−9.6 ± 1.5
	4.00	40.0	0.90 ± 0.02		
	4.00	50.0	2.4 ± 0.10		
			Benzyl tosylate		
90% acetone	3.00	30.0	0.63 ± 0.03	17.5 ± 0.50	−24.8 ± 1.6
	3.00	40.0	1.70 ± 0.10		
	3.00	45.0	2.67 ± 0.03		
	3.00	50.0	4.00 ± 0.01		
Sulfolane[c]	4.00	40.0	0.017 ± 0.0004	21.6 ± 0.40	−20.6 ± 1.5
	4.00	50.0	0.053 ± 0.001		
	4.00	60.0	0.143 ± 0.003		
DMSO[d]	2.00	20.0	33.3 ± 1.0	14.2 ± 0.10	−26.0 ± 1.0
	2.00	30.0	73.4 ± 1.0		
	2.00	40.0	166.8 ± 3.7		
CH_3OH	3.00	10.0	4.0 ± 0.20	14.1 ± 0.40	−28.4 ± 1.5
	3.00	20.0	10.2 ± 0.02		
	3.00	30.0	23.4 ± 0.04		
CH_3CH_2OH	2.00	30.0	9.16 ± 0.10	17.0 ± 0.20	−21.1 ± 1.0
	2.00	40.0	24.2 ± 0.20		
	2.00	50.0	55.7 ± 0.50		

[a] The uncertainties given are one standard deviation unit from the mean. [b] The uncertainties given are two standard deviation units from the mean. [c] Tetramethylene sulfone. [d] Dimethyl sulfoxide.

TABLE II

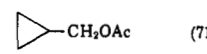
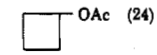
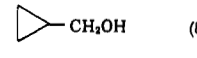
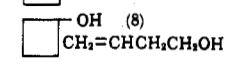
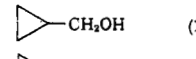
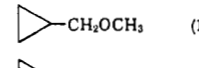
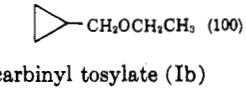
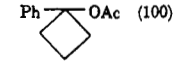
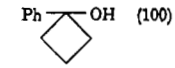
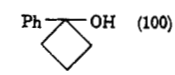
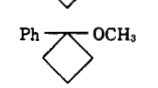
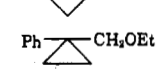
RELATIVE RATES OF THE ORGANIC TOSYLATES (ROTs) IN VARIOUS SOLVENTS

R	Relative rates, 25°					
	AcOH	Acetone[a]	Sulfolane	CH_3OH	DMSO	CH_3CH_2OH
Ethyl	1[b]	1	1	1[c]	1	1[b]
Benzyl	1,400[d]	128	27	670	300	520
Cyclopropylcarbinyl (Ia)	123,000[e]	1550	2,400	1000	72	675
1-Phenylcyclopropylcarbinyl (Ib)	205,000[e]	1170	21,000	1000	78	485

[a] Aqueous acetone, 90% (by volume). [b] From data of S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). [c] From data of R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [d] From data of S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951). [e] From data of ref. 1.

TABLE III

KINETIC BEHAVIOR AND SOLVOLYSIS PRODUCTS OF CYCLOPROPYLCARBINYL AND 1-PHENYLCYCLOPROPYLCARBINYL *p*-TOLUENESULFONATE IN VARIOUS SOLVENTS

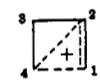
Solvent	Time[a]	% converted	Products[b] (%)
Cyclopropylcarbinyl tosylate (Ia)			
AcOH	20	65	 (71)  (24)
90% acetone	20	85	 (84)  (8)
Sulfolane	20	85	 (100)
DMSO[c]	10	100	
CH_3OH	10	100	 (100)
CH_3CH_2OH	10	100	 (100)
1-Phenylcyclopropylcarbinyl tosylate (Ib)			
AcOH[d]	10	100	 (100)
90% acetone	10	100	 (100)
DMSO	10	100	 (100)
CH_3OH	10	100	 (100)
CH_3CH_2OH	10	100	 (80)  (20)

[a] Half-lives. [b] Identification by g.l.p.c.; see Experimental for details. [c] S. G. Smith and S. Winstein [*Tetrahedron*, **3**, 317 (1958)] report that the solvolysis product for benzyl tosylate in anhydrous dimethyl sulfoxide is the O-alkylated dimethyl sulfoxide adduct which upon treatment with water rapidly undergoes hydrolysis to yield benzyl alcohol. In this work no attempt was made to characterize any possible DMSO adduct; instead, the more readily identifiable alcohol was isolated. [d] Solvent composition included sodium acetate.[1]

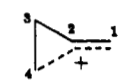
point for ethanol excluded, correlation coefficient = 0.98, β = 271°). It is possible to attribute such a dispersion of the enthalpy–entropy diagram for solvent as a variable to either too great a change in the solvation interaction mechanism for the deviating solvents or to a variable substrate contribution to ΔH^* or ΔS^* throughout the solvent series.

Lack of fit due to too great a change in medium effect is considered unlikely in view of the reasonable correlation obtained for 1-phenylcyclopropylcarbinyl tosylate. Association of the data scattering in Figure 1 with variable substrate contribution to the activation parameters is supported by the marked dependence of the product composition upon solvent (Table III). This interpretation is in keeping with variable transition state geometries necessary to account for the cyclopropylcarbinyl tosylate solvolysis products and suggests a variable interaction between the 1-ring position and the reaction site.

Previously, Winstein and Kosower[8] outlined the possible carbonium ion intermediates generated from cyclopropylcarbinyl derivatives. Germane to this work are the bicyclobutonium ion, II, and the unsymmetrical homoallylic ion, III. The main difference between the



II



III

two is the presence of significant 1,4 bonding in structure II with concomitant delocalization of charge at 1, 2 and 4 while in structure III, 1,4 bonding is essentially absent and hence most of the charge is localized at position 1. Such structures are consistent with the variable product distributions and isokinetic analysis or cyclopropylcarbinyl tosylate solvolyses.

(8) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959).

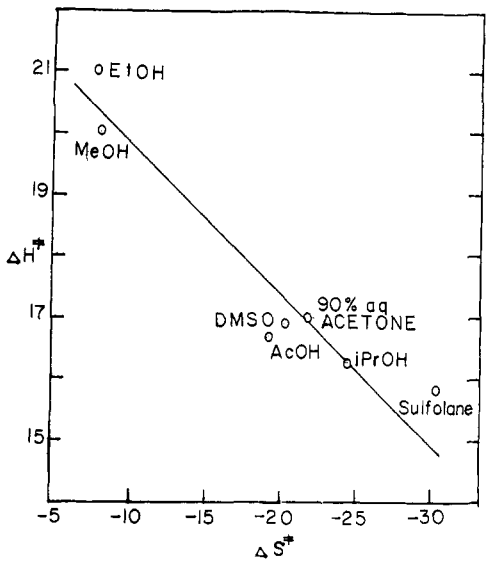


Figure 1.—Isokinetic correlation of cyclopropylcarbinyl *p*-toluenesulfonate activation parameters.

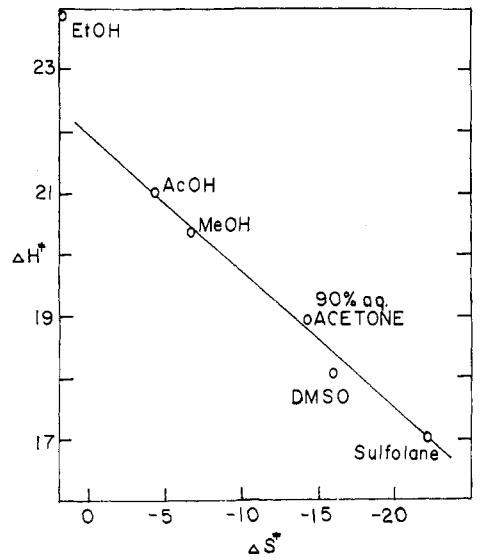


Figure 2.—Isokinetic correlation of 1-phenylcyclopropylcarbinyl *p*-toluenesulfonate activation parameters.

Driving Force for Neighboring Group Assistance.—Streitwieser[9] has successfully correlated solvolysis reactions of primary tosylates and secondary brosylates with Taft's σ^*-values and derived the driving forces for anchimeric assistance from the correlations. Application of this treatment to the present study should contribute further information concerning the effect of a 1-phenyl substituent on cyclopropylcarbinyl carbonium ion formation. This should be especially true if a correlation between structure and driving force is derived which includes Ib but not Ia.

Figures 3 and 4 represent such a relationship. It is readily apparent from these plots that the rate enhancement of Ib relative to unassisted solvolysis rates (Table IV) is linearly correlated with β-phenyl substituted compounds of similar structure in both solvents. This result emphasizes the importance of the phenyl ring as previously proposed[10] in the delocalization of the positive charge and conforms with the observation of

(9) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).
(10) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

TABLE IV

DRIVING FORCE FOR NEIGHBORING GROUP ASSISTANCE

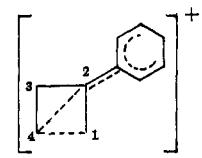
Tosylate	Solvent	Temp., °C.	log k/k_c[a]	L, kcal.
Neophyl[b]	AcOH	25	3.80	5.2
1-Phenylcyclopentylcarbinyl[c]			4.16	5.7
1-Phenylcyclohexylcarbinyl[c]			5.32	7.2
p-Methoxyneophyl[d]			6.64	9.1
1-Phenylcyclopropylcarbinyl[e]			8.80	12.0
Cyclopropylcarbinyl			8.00	11.0
Neophyl[b]	EtOH	75	2.88	4.6
p-Methoxyneophyl[d]			5.16	8.2
1-Phenylcyclopropylcarbinyl[e]			6.72	10.7
Cyclopropylcarbinyl[e]			6.24	9.9

[a] The values were obtained graphically by measuring the distances of the points above the correlation line (adjusted to pass through the point for the reference compound, neopentyl tosylate). [b] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952). [c] See ref. 10. [d] See ref. 5. [e] See ref. 1.

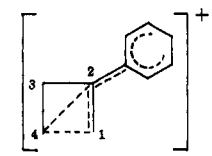
Streitwieser[11] that a correlation exists between the relative ease of forming a phenonium ion and the relative ease of forming a corresponding benzyl cation.

Another interesting feature of this neighboring group analysis is the contrast between the similarity of the L values and the dissimilarity of the product distribution in the two solvents, acetic acid and ethanol. Since the behavior of Ib is somewhat anomalous in ethanol the remaining discussion will be restricted to the nature of the carbonium ion intermediate generated in solvolysis of 1-phenylcyclopropylcarbinyl tosylate in the solvents employed other than ethanol.

The present data do not permit a rigorous description of such an intermediate but according to the Hammond postulate[12] the product structure will be a qualitative indication of the charge distribution in the carbonium ion intermediate. Therefore, in keeping with the solvolysis products reported for Ib in Table III, structure IV is proposed. The basic distinction between IV and V, the bicyclobutonium ion, is the degree of 1,2 bond-

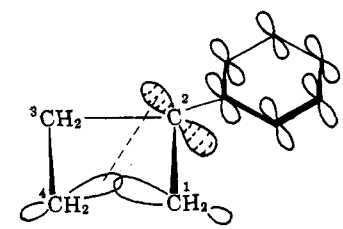


IV



V

ing. Localization of the positive charge at the methinyl carbon is due to increased overlap between the p-orbital on C-1 and the hybrid orbital on C-4 involved in the



weakened 2,4-σ bond. At the transition state, the developing p-orbital on C-2 is partially out of the plane of the ring, and is consequently near orthogonal to the incipient 1,4-σ bond. Thus, the localized positive

(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 384.
(12) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

charge on C-2 is stabilized by extended p-orbital overlap with the phenyl π-bond network at the expense of diminished 1,2-bond interaction due to orthogonality.

Experimental

Cyclopropylcarbinol was prepared in 86% yield by lithium aluminum hydride reduction of cyclopropanecarboxylic acid, b.p. 125° (760 mm.), lit.[3] b.p. 126° (760 mm.).

1-Phenylcyclopropylcarbinol was prepared in 85% yield by lithium aluminum hydride reduction of 1-phenylcyclopropanecarbonyl chloride, m.p. 32–33°, lit.[10] m.p. 32.5–33°.

Cyclopropylcarbinyl p-toluenesulfonate (Ia) was prepared according to published procedure.[3] The purities, calculated from "infinity" titers in ethanolysis reactions ranged from 85–93%. Vapor phase chromatography revealed that most of the impurity was accounted for by unreacted cyclopropylcarbinol; however, on standing overnight at 0°, the compound began to deteriorate by rearrangement to allylcarbinyl tosylate.

1-Phenylcyclopropylcarbinyl p-toluenesulfonate (Ib) was prepared according to established procedure,[10] m.p. 52° dec., lit.[10] m.p. 52° dec.

Rate measurements were accomplished by titration of the liberated p-toluenesulfonic acid with approximately 0.02 *N* methanolic sodium methoxide to a bromthymol blue end point. The base was frequently restandardized during the course of the work with little change in normality.

Solvents.—Ninety per cent (by volume) aqueous acetone was prepared from conductivity water and acetone purified by distillation from potassium permanganate. Sulfolane was supplied through the generosity of Phillips Petroleum Co., Bartlesville, Oklahoma, and was purified by redistillation just prior to use. Dimethyl sulfoxide was purified by drying over 4A Molecular Sieves and distillation, m.p. 18.0–18.5°. Absolute methanol was prepared by distillation from magnesium turnings and absolute ethanol was prepared according to the method of Fieser.[13a]

Treatment of Kinetic Data.—The thermodynamic activation parameters and correlation coefficients for isokinetic treatments were obtained by IBM 1620 computer regression analysis.

Product Studies. A. Cyclopropylcarbinyl p-Toluenesulfonate Solvolysis Products. 1. In 90% Aqueous Acetone.—Cyclopropylcarbinyl p-toluenesulfonate (Ia, 1.5 g.) was solvolyzed in 25 ml. of 90% aqueous acetone at 25° for 20 half-lives. The material was added to ice–water (50 ml.) and extracted with five 15-ml. portions of methylene chloride. The combined methylene chloride extracts were dried over anhydrous sodium sulfate and most of the solvent was removed by distillation. Injection of a sample of this solution into a vapor fractometer (Tide,[13b] 145°) gave, in addition to a solvent peak, two small peaks A and B and one large peak C. A sample of authentic allylcarbinol[14] gave a chromatogram with a retention time identical with peak A and, similarly, samples of authentic cyclobutanol[2] and cyclopropylcarbinol[3] gave chromatograms with retention times identical with peaks B and C, respectively.

2. In Dimethyl Sulfoxide.—Cyclopropylcarbinyl p-toluenesulfonate (Ia, 1.6 g.) was solvolyzed in 25 ml. of dry DMSO at 25° for ten half-lives. The material was worked up as before and analysis by g.l.p.c. (Tide,[13b] 145°) revealed the presence of a single product peak with a retention time identical with that of authentic cyclopropylcarbinol.[3]

3. In Methanol.—Cyclopropylcarbinyl p-toluenesulfonate (Ia, 2.0 g.) was solvolyzed in 25 ml. of absolute methanol at 30° for ten half-lives. The material was worked up as before and analysis by g.l.p.c. (dioctyl phthalate, 82°) revealed the presence of a single product peak with a retention time identical with that of authentic methyl cyclopropyl carbinyl ether.

4. In Ethanol.—Cyclopropylcarbinyl p-toluenesulfonate (Ia, 2.0 g.) was solvolyzed in 25 ml. of ethanol at 30° for ten half-lives. The material was worked up as before and analysis by g.l.p.c. (dioctyl phthalate, 82°) revealed the presence of a single product peak with a retention time identical with that of authentic ethyl cyclopropylcarbinyl ether.[3]

B. 1-Phenylcyclopropylcarbinyl p-Toluenesulfonate Solvolysis Products. 1. In 90% Aqueous Acetone.—1-Phenylcyclopropylcarbinyl p-toluenesulfonate (Ib, 1.2 g.) was solvolyzed in 25 ml. of 90% acetone at 25° for 20 half-lives. The material was worked up as before and analysis by g.l.p.c. (silicone rubber, 165°) revealed the presence of a single product peak with a retention time identical with that of authentic 1-phenylcyclobutanol.[10]

2. In Dimethyl Sulfoxide.—1-Phenylcyclopropylcarbinyl p-toluenesulfonate (Ib, 1.5 g.) was solvolyzed in 25 ml. of dry dimethyl sulfoxide at 25° for 20 half-lives. After the usual work up, analysis by g.l.p.c. (Tide,[13b] 207°) gave a chromatogram identical with the exception of the solvent peaks to that obtained for 1-phenylcyclobutanol (under these conditions, the al-

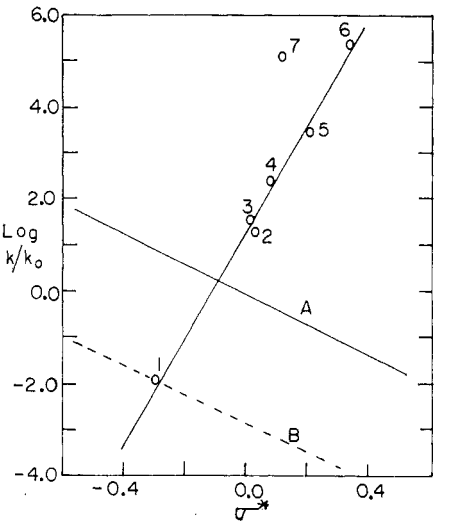


Figure 3.—Correlation of primary carbinyl tosylate acetolysis rates with polar substituent constants, σ^*: (1) neopentyl tosylate, (2) neophyl tosylate, (3) 1-phenylcyclopentylcarbinyl tosylate, (4) 1-C-phenylcyclohexylcarbinyl tosylate (5) p-methoxyneophyl tosylate, (6) 1-phenylcyclopropylcarbinyl tosylate, and (7) cyclopropylcarbinyl tosylate. Line A represents the correlation line obtained from data of Streitwieser.[9] Line B represents the correlation line adjusted to pass through the point for reference compound, neopentyl tosylate.

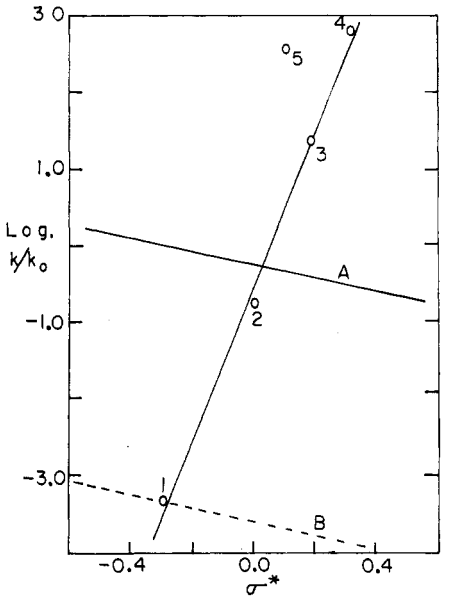


Figure 4.—Correlation of primary carbinyl tosylate ethanolysis rates with polar substituent constants, σ^*: (1) neopentyl tosylate, (2) neophyl tosylate, (3) p-methoxyneophyl tosylate, (4) 1-phenylcyclopropylcarbinyl tosylate, and (5) cyclopropylcarbinyl tosylate. Line A represents the correlation line obtained from data of Streitwieser.[10] Line B represents the correlation line adjusted to pass through the point for the reference compound, neopentyl tosylate.

(13) (a) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed. rev., D. C. Heath and Co., Boston, Mass., 1957, p. 285. (b) Detergent made by Procter and Gamble.

(14) E. Renk and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 878 (1961).

cohol was partially dehydrated, yielding 1-phenylcyclobutene, a behavior in accord with previously observed behavior of the acetate[10]).

3. In Methanol.—1-Phenylcyclopropylcarbinyl *p*-toluenesulfonate (Ib, 1.2 g.) was solvolyzed in 25 ml. of absolute methanol at 25° for 20 half-lives. After the usual work-up, analysis by g.l.p.c. (Tide,[13b] 195°) revealed the presence of a single product peak with a retention time identical with that of authentic methyl 1-phenylcyclobutyl ether.

4. In Ethanol.—1-Phenylcyclopropylcarbinyl *p*-toluenesulfonate (Ib, 1.5 g.) was solvolyzed in 25 ml. of absolute ethanol at 35° for 15 half-lives. After the usual work-up, analysis by g.l.p.c. (Tide,[13b] 200°) revealed the presence of one large peak with a retention time identical with that of authentic 1-phenylcyclopropylcarbinyl ether and a smaller peak with a retention time identical with that of authentic ethyl 1-phenylcyclobutyl ether.

Preparation of Reference Materials. Allylcarbinol was prepared in 64% yield by lithium aluminum hydride reduction of 3-butenoic acid, b.p. 112–113° (760 mm.), lit.[14] b.p. 110–1111° (760 mm.).

Cyclobutanol was prepared by acid-catalyzed ring expansion of cyclopropylcarbinol,[2] b.p. 122–124° (760 mm.).

Methyl cyclopropylcarbinyl ether resulted when dimethyl sulfate (2.0 g., 16 mmoles) in dry *n*-butyl ether (10 ml.) was added dropwise to the sodium salt of cyclopropylcarbinol (prepared from 2.0 g., 28 mmoles, of alcohol and 2.0 g., 30 mmoles, of sodium hydride in mineral oil) stirred in dry *n*-butyl ether (30 ml.). After cooling, the material was poured onto ice and acidified with dilute hydrochloric acid, and the ether layer was separated. Drying over anhydrous sodium sulfate and distillation yielded the ether, 0.7 g., b.p. 80–81° (760 mm.).

Anal. Calcd. for $C_6H_{10}O$: C, 69.72; H, 11.70. Found: C, 68.95; H, 12.00.

Ethyl cyclopropylcarbinyl ether was prepared according to published procedure,[3] b.p. 99–100° (760 mm.).

1-Phenylcyclobutanol was prepared in 91% yield by the lithium aluminum hydride reduction of 1-phenylcyclobutyl acetate, m.p. 40–41°, lit.[10] m.p. 40–41°.

Methyl 1-phenylcyclobutyl ether resulted when dimethyl sulfate (0.5 g., 6 mmoles) in dry benzene (10 ml.) was added dropwise to the sodium salt of 1-phenylcyclobutanol (prepared from 1.5 g., 10 mmoles, of alcohol and 0.5 g., 11 mmoles, of sodium hydride in mineral oil) stirred in dry benzene (25 ml.). After cooling, the material was poured onto ice, and the benzene layer was separated. The aqueous layer was extracted with three 30-ml. portions of ether and the combined organic phases were dried over anhydrous sodium sulfate. Distillation yielded the ether, 0.8 g., b.p. 36° (0.02 mm.).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.59; H, 8.71.

Ethyl 1-phenylcyclopropylcarbinyl ether resulted when the sodium salt of 1-phenylcyclopropylcarbinol (prepared from 4.0 g., 27 mmoles, of alcohol and 1.5 g., 30 mmoles, of sodium hydride in mineral oil) in dry benzene (40 ml.) and ethyl *p*-toluenesulfonate (5.4 g., 27 mmoles) were stirred together at reflux temperature for 24 hr. After cooling, and the usual work-up, distillation yielded the ether, 2.2 g., b.p. 60–62° (0.3 mm.).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.71; H, 9.40.

A forecut was analyzed by g.l.p.c. and revealed in addition to ethyl 1-phenylcyclopropylcarbinyl ether an equivalent amount of ethyl 1-phenylcyclobutyl ether.

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The Mechanism of the Acid-Catalyzed Rearrangement of N-Arylaminomethyl Aryl Sulfides

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Evidence is presented to indicate that the condensation of aromatic thiols, formaldehyde, and aromatic amines in the presence of strong acid results first in the formation of the intermediate products, N-arylaminomethyl aryl sulfides (I) which then rearrange intermolecularly to *p*-aminobenzyl aryl sulfides (II), a process resembling closely the acid-catalyzed rearrangement of diazoaminobenzenes to *p*-aminoazobenzenes. Two mechanisms consistent with the experimental data are indicated for the acid-catalyzed reaction of aromatic thiols and formaldehyde with primary and secondary amines, and also the mechanism of the condensation with tertiary amines. It is conjectured that a resonance-stabilized sulfonium–carbonium ion is the reactive species that migrates from the nitrogen atom to the *para* position of the aromatic amine.

Recently Lau and Grillot[2] have found that N-arylaminomethyl aryl sulfides (I), prepared by the condensation of aromatic thiols, formaldehyde, and aromatic amines, rearrange smoothly and in good yield to *p*-aminobenzyl aryl sulfides (II) in the presence of acid. These benzyl sulfides can also be prepared in nearly the same yield by the condensation of the thiophenol, formaldehyde, and aromatic amine in an acid solution. The fact that the yields of the *p*-aminobenzyl aryl sulfides II are practically the same by either procedure suggests that N-arylaminomethyl aryl sulfides (I) are the intermediate products in the formation of *p*-aminobenzyl aryl sulfides (II) from thiophenols, formaldehyde, and aromatic amines. This is demonstrated by the isolation of over 40% of recrystallized N-methyl-N-phenylaminomethyl *p*-chlorophenyl sulfide (Ia) from the reaction mixture of *p*-chlorothiophenol, formaldehyde, N-methylaniline, and hydrochloric acid during the first 5 min. of the reaction carried out at 40°, while, with the less reactive *o*-chloroaniline, under similar conditions, over 80% of N-(*o*-chlorophenyl)-aminomethyl *p*-chlorophenyl sulfide (Ib) is isolated.

Furthermore, it is found that, if N,N-dimethylaniline, which cannot form an intermediate Mannich base, is refluxed with thiophenol or *p*-chlorothiophenol, formaldehyde, and hydrochloric acid in ethanol, a yield of only 15–33% of the N,N-dimethyl-*p*-aminobenzyl aryl sulfides (IIc and IId) are obtained. However, if the reaction is carried out in the presence of 0.5 *M* ratio of N-methyl-*p*-toluidine, the yield is increased to over 80%. Similarly β-naphthol, which does not react with thiophenol and formaldehyde in the presence of acid,[3] was found to react smoothly to give 65% of 1-phenylthiomethyl-2-naphthol (III) when a 0.5 *M* ratio of N-methyl-*p*-toluidine is added to the reaction mixture. Obviously, these reactions can only occur in such a manner that first the Mannich base N-methyl-N-

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(2) P. T. S. Lau and G. F. Grillot, *J. Org. Chem.*, **28**, 2763 (1963).

(3) F. Poppelsdorf and S. J. Holt, *J. Chem. Soc.*, 1124 (1954).