chlorate ion since chloroform forms an emulsion under these conditions. The infinity point (100% reaction) for the very slow runs was obtained from tubes placed in a 100° thermostat for at least 20 half-lives. For runs in the presence of 0.1 M salt, 2.4 g. of lithium perchlorate trihydrate was added to the reaction mixture.

The hydrolysis of methyl bromide in the presence of hydroxide ion was accomplished in a similar manner except that the reaction mixture consisted of 108.9 ml. of 0.973 N sodium hydroxide and 1.1 ml. of the stock solution of methyl bromide in acetone.

The reaction of methyl bromide in the presence of azide ion was conducted in a similar fashion. The reaction mixture consisted of 715 mg. (0.011 mole) of sodium azide, 108.9 ml. of water and 1.1 ml. of the stock solution of methyl bromide. The contents of the tubes, after shaking with chloroform, were treated with 5.0 ml. of 0.04 N silver nitrate, 10 drops of ferric alum indicator, 4 ml. of concentrated nitric acid to dissolve the silver azide and titrated for excess silver ion with 0.114 N potassium thiocyanate. The tubes for 100% reaction were allowed to stand for at least 10 half-lives at 49.8° or placed in a steam-bath to hasten the reaction. Identical results were obtained in either case.

The reactions of methyl bromide in 50% water–50% acetone were conducted similarly.

The same procedure was used for the reaction of methyl bromide with aniline except that the reaction mixture consisted of 1.394 g. (0.015 mole) of aniline, 74 ml. of acetone, 75 ml. of water and 1 ml. of the stock solution of methyl bromide.

The reaction mixture for the hydration of glycidol consisted of 100 ml. of 0.1783 N sodium hydroxide and 755 mg. (0.0102 mole) of glycidol. Aliquots (5 ml.) were brought to a brom thymol blue end-point with 0.05 N nitric acid and mixed with 5.0 ml. of a solution of 2.1 M magnesium bromide and 0.172 N sulfuric acid.[20] After at least 10 hr. this new solution was titrated for remaining acid with 0.1783 N sodium hydroxide.

Acetyl chloride was hydrolyzed in a 100-ml. round-bottomed flask equipped with sealed stirrer and glass-stoppered side-arm. The reaction solvent, 75 ml. of acetone and 25 ml. of water, was mixed in the cell and the acetyl chloride blown in directly from a pipet. Aliquots (10 ml.) were shaken with 20 ml. of chloroform and the aqueous portion titrated for chloride ion with mercuric nitrate. It was necessary to maintain the pipet and chloroform at or below

(20) O. F. Lubatti, *J. Soc. Chem. Ind.*, **54**, 424T (1935).

the temperature of the reaction to prevent warming of the aliquots.

Benzoyl chloride and bromide and benzenesulfonyl chloride were hydrolyzed in the 100-ml. round-bottomed cell. When benzoyl chloride was hydrolyzed in the presence of acetic acid, the reaction mixture consisted of 0.457 ml. of 17.5 N acetic acid, 49.6 ml. of water and 45 ml. of acetone. The benzoyl chloride was added in 5 ml. of pre-cooled acetone. Aliquots (10 ml.) were shaken with 20 ml. of chloroform and the aqueous portions titrated for chloride ion with mercuric nitrate. When nitric acid was present, the solvent consisted of 3 ml. of 1 N nitric acid, 47 ml. of water, 45 ml. of acetone and 5 ml. of acetone containing the benzoyl chloride. With acetate ion present, the reaction mixture contained 8 ml. of a 0.5 M sodium acetate–0.5 M acetic acid buffer, 42 ml. of water, 45 ml. of acetone and 5 ml. of acetone with the benzoyl chloride. The hydrolysis of benzenesulfonyl chloride was conducted in 50 ml. of water and 50 ml. of acetone. When 0.1 M salt or acid was present, 5 ml. of 2 N lithium perchlorate or perchloric acid replaced 5 ml. of the water in the solvent. When 0.04 M lithium perchlorate was present, a larger cell was used and the solvent consisted of 4 ml. of 2 N lithium perchlorate, 96 ml. of water, 90 ml. of acetone and 10 ml. of acetone containing the acid chloride.

Hydrolyses of all the acid halides in the presence of base were conducted in a 200-ml. round-bottomed flask equipped with mechanical stirrer and side-arm. The reaction mixture used for all runs consisted of 40 ml. of 0.2 M boric acid, 22.4 ml. of 0.1783 N sodium hydroxide, 37.6 ml. of water and 100 ml. of acetone. Aliquots (20 ml.) were shaken with 20 ml. of chloroform and titrated for halide ion. When the buffer concentration was halved to investigate the effect of boric acid and monobasic sodium borate, the reaction mixture consisted of 20 ml. of 0.2 M boric acid, 11.2 ml. of 0.1783 N sodium hydroxide, 68.8 ml. of water and 100 ml. of acetone.

The reactions of acid halides with aniline were conducted in the 100-ml. round-bottomed cell described previously. Solutions containing a constant concentration of 1.1 × 10^{-4} M aniline were prepared from 8 ml. of 1 N nitric acid, 42 ml. of water, 50 ml. of acetone and 464 mg. (0.005 mole) of aniline. Solutions containing 1.1 × 10^{-2} M aniline were prepared from 4 ml. of 1 N nitric acid, 46 ml. of water, 50 ml. of acetone and 464 mg. (0.005 mole) of aniline.

Table VI gives sample kinetic data.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. XIV. Participation in Solvolysis of Some Primary Benzenesulfonates[1]

BY S. WINSTEIN, C. R. LINDEGREN, H. MARSHALL AND L. L. INGRAHAM

The study of the solvolysis of a series of primary benzenesulfonates has supplied evidence on: (a) the magnitude of anchimeric assistance to ionization in the pinacol rearrangement; (b) the participation of β-aryl in solvolysis of PβPα systems in the common solvents. The data show that the magnitude of anchimeric assistance in the pinacol rearrangement may be large and can compare with that in the Wagner–Meerwein rearrangement. A β-methoxy group has an effect on the driving force due to participation approximately equivalent to that of a phenyl group or two methyl groups. Solvolysis of 2-p-anisylethyl p-toluenesulfonate is relatively rapid and the data indicate that p-anisyl participation in solvolysis of the toluene-sulfonate is well developed in acetic and formic acid solvents. The present data together with previous data indicate that the effects of α- and β-methyl groups on free energy of activation of anchimerically assisted ionization are additive with neighboring p-anisyl and phenyl. The parameters for the effect per α- or β-methyl group are compared for neighboring p-anisyl, phenyl and the neighboring functional groups, I, Br, OH, OCH₃, O⁻.

In the present article are reported the results of a study of the solvolysis of several primary benzenesulfonates of interest in connection with participation by neighboring carbon.[2]

In connection with the Wagner–Meerwein rear-

(1) Much of the material in this paper was presented in summary at Montpellier, April 26. 1950 [*Bull. soc. chim.*, **18**, 55 (1951)]. Taken from Ph.D. theses of C. R. Lindegren, U. C. L. A., 1950, and H. Marshall, U. C. L. A., 1952.

(2) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

rangement, it is clear that rate may be very substantially enhanced by participation of carbon in the rate-determining ionization[2] (I). This anchi-

I   II   III
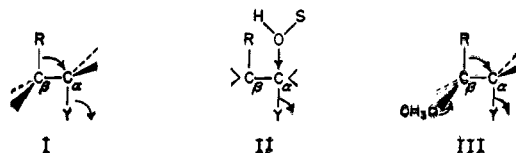
meric[3,4] assistance may be measured by the driving force[2,5] L due to participation, defined by equation

$$L = RT \ln k/k_c \qquad (1)$$

1, where k is the rate constant for ionization with participation and k_c is the estimated rate constant of ionization with neither anchimeric assistance (I) nor nucleophilic assistance from solvent[6] (II). Similarly large driving forces may be expected in the pinacol type of rearrangement (III), where the electronic situation is analogous to that in the Wagner–Meerwein case,[2,4] a β-substituent such as methoxyl or hydroxyl (III) being available, however, to determine the nature of the final product. Some of the present results furnish information on the magnitude of anchimeric assistance in the pinacol rearrangement.

While the driving forces due to neighboring group participation are highest for primary systems[2,7] (P_α), it is frequently observed, especially where C_β is also unsubstituted (except for the neighboring group), that is, in systems of the $P_\beta P_\alpha$[7] type, that the rate constant of solvolysis with nucleophilic solvent participation (II) exceeds k_c more than does the anchimerically assisted ionization rate. Thus neighboring group participation fails to compete with solvent participation. The present results show what the indications are from kinetics regarding the importance of β-aryl participation in solvolysis of $P_\beta P_\alpha$ systems. The data are treated in conjunction with previous data on more substituted β-aryl systems in exploring the semiquantitative aspects of the dependence of the rate of anchimerically assisted ionization on α- and β-methyl substitution.

Results

As in the previous work[2,5,7] we preferred benzenesulfonates, and the substances reported on in the present article are of the type IV, with both neighboring phenyl and methoxyl, and type V, with neighboring phenyl, o-anisyl and p-anisyl.
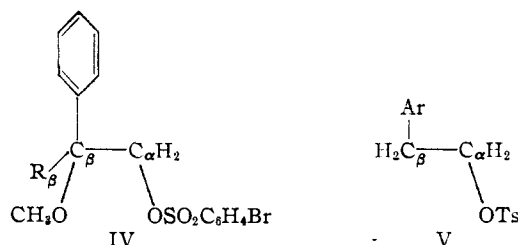
The esters IV and V were prepared from the corresponding glycol monomethyl ethers or 2-aryleth-

(3) This adjective (from the Greek "anchi" and "meros"), meaning pertaining to the neighboring or adjacent part, has been suggested to us by Dr. A. P. McKinlay, Professor Emeritus in the Classics, U. C. L. A., for use in connection with neighboring group participation. Thus we have anchimeric electron supply or electron release. This term applies to neighboring carbon, hydrogen and functional groups, whether the participation involves electrons besides the β-bonding electron-pair (e.g., Br, vinyl, phenyl) or not (e.g., H, R). Further discussion is given elsewhere.[4]
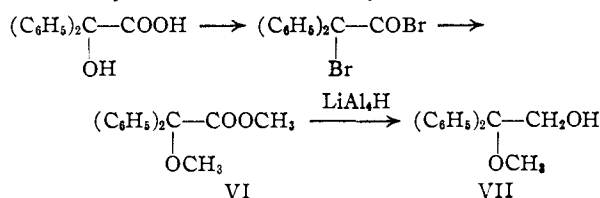
(4) S. Winstein and L. L. Ingraham, being submitted to THIS JOURNAL.

(5) S. Winstein, E. Grunwald and L. L. Ingraham, ibid., 70, 821 (1948).

(6) S. Winstein, E. Grunwald and H. W. Jones, ibid., 73, 2700 (1951).

(7) S. Winstein and E. Grunwald, ibid., 70, 828 (1948).

anols. 2-Methoxy-2-phenylethanol was available from acid-catalyzed opening of styrene oxide with methanol[4]; the 2-methoxy-2,2-diphenylethanol (VII) was prepared by reduction of methyl β-methoxy-β,β-diphenylacetate (VI) with lithium aluminum hydride. The necessary ester VI was avail-

$$(C_6H_5)_2C\text{—COOH} \longrightarrow (C_6H_5)_2C\text{—COBr} \longrightarrow$$
$$\quad\quad |\qquad\qquad\qquad\qquad |$$
$$\quad\quad OH \qquad\qquad\qquad\quad Br$$

$$(C_6H_5)_2C\text{—COOCH}_3 \xrightarrow{\ \text{LiAl}_4\text{H}\ } (C_6H_5)_2C\text{—CH}_2OH$$
$$\quad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\quad\quad OCH_3 \qquad\qquad\qquad\qquad\quad OCH_3$$
$$\qquad\quad VI \qquad\qquad\qquad\qquad\qquad VII$$

able from benzilic acid by the general procedure of Klinger and Nickell.[8]

In the solvolysis of the β-methoxy-substituted bromobenzenesulfonates IV, satisfactory first-order rate constants were obtained in acetic and formic acids with 2-methoxy-2-phenylethyl p-bromobenzenesulfonate (IV, R_β = H), and these are summarized in Table I. In acetic acid not containing potassium acetate, a rapidly decreasing first-order rate constant was obtained with 2-methoxy-2,2-diphenylethyl p-bromobenzenesulfonate (IV, R_β = C_6H_5). This was possibly due to some acid-catalyzed reaction involving the tertiary methoxyl group; inclusion of 0.05 M potassium acetate in the acetic acid solvent disposed of the difficulty, good first-order constants now being obtained. A sample run is illustrated in Table II and the data are summarized in Table I.

With 2-methoxy-2,2-diphenylethyl p-bromobenzenesulfonate (IV, R = C_6H_5), the solvolysis was also followed in 80% dioxane, ca. 0.05 M in potassium acetate. In this solvent at 75°, the rate was approximately a third as fast as in acetic acid, good first-order behavior being observed (Table I).

It is quite clear that the solvolysis rate constants for IV are fairly close measures of rates of reaction which involve phenyl group migration, at least at some stage. For 2-methoxy-2-phenylethyl p-bromobenzenesulfonate (E, Table III), we regard this as a fair approximation in view of the chemistry of the corresponding iodide.[1,4] For 2-methoxy-2,2-diphenylethyl p-bromobenzenesulfonate (F, Table III), this is clear from the product of solvolysis in 80.78% dioxane, buffered with potassium acetate. There was obtained an 89% yield of desoxybenzoin X, identified by melting point and mixed melting
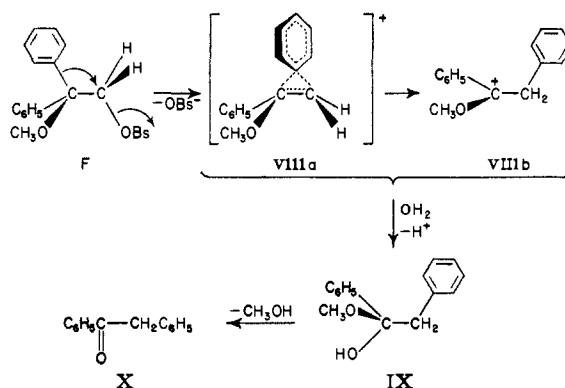
(8) H. Klinger and G. Nickell, Ann., 390, 365, 371 (1912).

TABLE I
SUMMARY OF RATE CONSTANTS

Compound	Solvent	Concn., M	Other solute	Temp., °C.	k, sec.$^{-1}$
C₆H₅CH(OCH₃)CH₂OBs	AcOH	0.055		74.73	(7.15 ± 0.14) × 10⁻⁷
	HCOOH	.030	0.0315 M NaOCHO	74.52	(4.8 ± 0.2) × 10⁻⁶
(C₆H₅)₂C(OCH₃)CH₂OBs	AcOH	.051	.0532 M KOAc	75.00	(3.35 ± 0.03) × 10⁻⁵
	80.78% dioxane	.051	.0550 M KOAc	75.00	(1.03 ± 0.03) × 10⁻⁵
	80.78% dioxane	.038-0.041	.039 M KOAc	47.95	(4.0 ± 0.8) × 10⁻⁷
C₆H₅CH₂CH₂OTs	EtOH	.023		75.01	(7.08 ± 0.06) × 10⁻⁶
	AcOH			49.7ᵃ	1.59 × 10⁻⁸
	AcOH	.037-0.041		75.01	(2.88 ± 0.06) × 10⁻⁷
	AcOH	.02557	.03699 M KOAc	75.01ᵇ	(4.90 ± 0.36) × 10⁻⁷
	AcOH	.01738	.03751 M KOAc	75.01ᵇ	(5.12 ± 0.10) × 10⁻⁷
	AcOH	.024-0.027		99.62	(3.31 ± 0.07) × 10⁻⁶
	HCOOH			25.1ᶜ	1.8 × 10⁻⁷
	HCOOH	.067		75.01	(3.94 ± 0.08) × 10⁻⁵
	HCOOH	.074		74.62	(3.59 ± 0.04) × 10⁻⁵
o-CH₃OC₆H₄CH₂CH₂OTs	EtOH	.029		75.00	(8.25 ± 0.09) × 10⁻⁶
	AcOH	.028		75.00	(6.88 ± 0.21) × 10⁻⁶
	AcOH	.036-0.040		99.69	(8.96 ± 0.35) × 10⁻⁵
	HCOOH	.063-0.070		75.01	(1.75 ± 0.09) × 10⁻³
p-CH₃OC₆H₄CH₂CH₂OTs	EtOH	.022		75.01	(1.35 ± 0.03) × 10⁻⁵
	AcOH			49.7ᵃ	4.34 × 10⁻⁷
	AcOH	.018-0.029		74.97	(8.38 ± 0.14) × 10⁻⁶
	AcOH	.02843	.06989 M KOAc	75.02ᵇ	(2.65 ± 0.12) × 10⁻⁵
	AcOH	.03417	.04579 M KOAc	75.02ᵇ	(2.52 ± 0.14) × 10⁻⁵
	AcOH	.024		99.58	(1.01 ± 0.04) × 10⁻⁴
	HCOOH	.043-0.052		50.01	(1.46 ± 0.04) × 10⁻⁴
	HCOOH	.073-0.075		75.01	(1.77 ± 0.14) × 10⁻³

ᵃ Extrapolated from data at higher temperatures. ᵇ Calculated first-order reaction rate constants. Especially with C₆H₅CH₂CH₂OTs, a substantial part of reaction could be bimolecular involving acetate ion. ᶜ Extrapolated, assuming $\Delta H\ddagger = 21.5$ kcal./mole (estimated with $\Delta S\ddagger$ identical to that in AcOH).

point with an authentic specimen. This is written as arising from one or more intermediates,[4] e.g., VIIIa,b, through the hemiacetal IX although alkyl-oxygen cleavage in the methoxyl group of VIIIb is conceivable and we have no evidence on this point.[4]

TABLE II
RATE OF ACETOLYSIS OF 0.05016 M β,β-DIPHENYL-β-METHOXYETHYL p-BROMOBENZENESULFONATE IN AcOH (0.05321 M KOAc) AT 74.99°

Time, min.	ROBs, meq.	$10^5 k$, sec.$^{-1}$
0	0.2410	
30	.2267	3.40
60	.2135	3.37
90	.2008	3.38
120	.1885	3.41
150	.1771	3.42
532	.0843	3.29
	Mean	3.38 ± 0.03

The solvolyses of the 2-arylethyl p-toluenesulfonates V showed good first-order behavior, in general, especially in ethanol and formic acid, the rate constants being summarized in Table I. Also included in Table I for comparison purposes are several rate constants extrapolated from data at other temperatures. With the 2-anisylethyl esters K and L (Tables IV and V) in acetic acid there was a downward trend of the order of magnitude of 10% in the first-order rate constants during a run. This has not yet been investigated further, but it is not serious for our present purposes.

The product of formolysis of 2-p-methoxyphenyl-ethyl p-toluenesulfonate L was examined, the formolysis being carried out in formic acid, 0.04% in water, and containing sodium formate (0.10 M) equivalent to the toluenesulfonate ester. Judging by the behavior of toluenesulfonate L toward addition of acetate ion to acetic acid (Table I) and ethyl toluenesulfonate H toward addition of formate ion to formic acid,[9] any bimolecular contribution, involving formate ion, to the formolysis of L is negligible. The product of the first-order formolysis of L gave negative phenolic and olefinic tests before and after reduction with lithium aluminum hydride. Substantially pure 2-p-anisylethanol, m. p. 27–28°, was obtained, its infrared spectrum being essentially identical with that of the synthetic specimen over the entire range from 7.4 to 12.0 μ. The infrared spectral comparison is shown further in Fig. 1 in the region from 10 to 12 μ where the spectrum of 2-p-methoxyphenylethanol differs greatly from that of 1-p-methoxyphenylethanol which we had regarded as a possible contaminant. From the effect of 10% of 1-p-methoxyphenylethanol on the spectrum, it is clear that only negligible amounts of this contaminant could be present.

Discussion

Comparison of Wagner–Meerwein and Pinacol Rearrangements.—In Table III, rates of solvolysis of the methoxy-substituted ethyl p-bromobenzenesulfonates E and F are compared with that of the neopentyl arylsulfonate[2] A, just as in the discussion of the Wagner–Meerwein rearrangement.[2] As shown in Table III, 2-methoxy-2-phenylethyl E

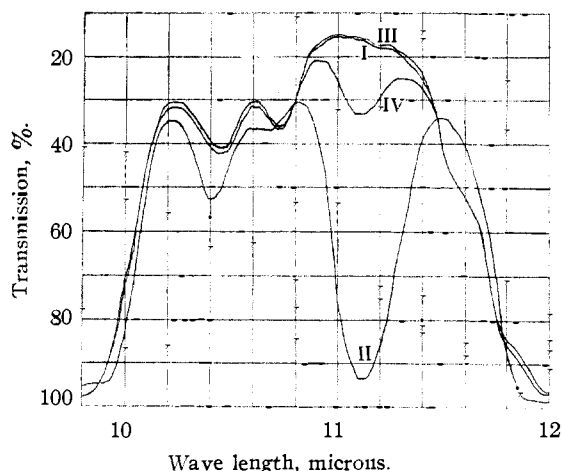(9) S. Winstein and H. Marshall, THIS JOURNAL, 74, 1120 (1952).

Fig. 1.—Infrared spectra of 2-p-methoxyphenylethanol and possible contaminant: I, pure 2-p-methoxyphenyl-ethanol; II, pure 1-p-methoxyphenylethanol; III, 50° formolysis product of 2-p-methoxyphenylethyl p-toluenesulfonate; IV, synthetic mixture: 0.01 ml. of 1-p-methoxyphenylethanol per 0.1 ml. of 2-p-methoxyphenylethanol.

is 3.5 times and 2-methoxy-2,2-diphenylethyl F is 160 times as reactive as neopentyl A in acetic acid at 75°. These values need to be corrected for the rate-depressing effect on k_c of both the phenyl and methoxyl groups. For phenyl we have used the factor of ca. ten previously employed,[2] and for methoxyl we have used the rough factor of ca. 10^2 previously estimated[5] in connection with neighboring functional group participation. On this basis, the estimated values of k/k_c become 3.5×10^3 and 1.6×10^6 for E and F, respectively, these values being lower limits due to possible anchimeric enhancement of neopentyl ionization rate.[2,9,10] On this basis, E is at least 3500 times and F at least a million times as reactive as they would be if ionization proceeded without anchimeric assistance. It is apparent that driving forces may be large in the pinacol rearrangement just as in the Wagner–Meerwein phenomenon.

(10) A more refined treatment, important for the discussion of relative migration or participation aptitudes, would consider all three possible conformations in a case such as E
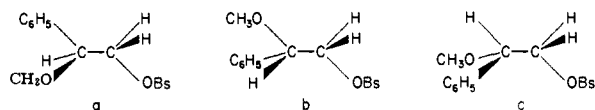
Each conformation corresponds to a different k_c. For example the rate-depressing factor of 10^2 for a methoxyl group previously[5] estimated is for a *trans*-methoxyl group, as in conformation b. It will be somewhat larger for a "skew" methoxyl group, as in conformations a and c. Similarly, the factor for phenyl can differ between conformations.

For the driving force L due to a certain participation, one has a choice of definitions. For k_c we could take: (i) a weighted value based on the relative amounts of the conformational isomers; (ii) one of the k_c values arbitrarily; (iii) the k_c value for the conformation corresponding to the participation in question, for example, conformation a in the case of phenyl participation. If also, in the latter case, the rate constant, k_r of ionization with participation is divided by the fraction of reactant existing as conformation a, the derived driving force would relate to the conformational isomer a.

No such refinements have been included in the rough comparisons here reported, although they are important in other connections. Steric factors can affect the relative concentrations of conformational isomers and the driving forces due to the respective participations displayed by the conformational isomers.

TABLE III

RELATIVE ACETOLYSIS RATES OF PRIMARY ARYLSULFONATES

		Rel. k AcOH 75°	Estimated k/k_c
A	$(CH_3)_2$—$\overset{\overset{\displaystyle CH_3}{|}}{C}$—$CH_2OBs$	1	1
B	CH_3—CH—CH_2OBs	40	4×10^2
C	CH_3—$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}$—$CH_2OBs$	250	2.5×10^3
D	C_6H_5CH—CH_2OBs	34	3.4×10^3
E	CH_3OCH—CH_2OBs	3.5	3.5×10^3
F	C_6H_5—$\overset{}{\underset{\underset{\displaystyle CH_3O}{|}}{C}}$—$CH_2OBs$	1.6×10^2	1.6×10^6
G	$(C_6H_5)_2C$—CH_2OBs	4.0×10^3	4×10^6

In fact, the two phenomena may be compared in this respect, and this is done in Table III.
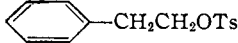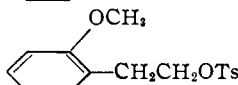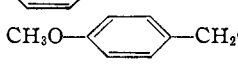
For comparison purposes, Table III includes rates (compared to neopentyl A) of solvolysis of several primary arylsulfonates which possess a migrating β-phenyl group, 2,2,2-triphenylethyl[2] G, 2,2-diphenylethyl[2] D, 2,2-dimethyl-2-phenyl-ethyl[2] C, and 2-phenyl-1-propyl[11,12] B. For A, C, D and G, as for E and F, actual solvolysis rate constants were used for comparison. For B, where "internal return"[11,13] is visible, and the kinetics permit evaluation of k_p, a direct solvolysis rate constant, and k_r, the rate constant for rearrangement of B to benzylmethylcarbinyl ester, the sum, $k_r + k_p$, was employed in the comparison. The value, $k_r + k_p$, measures total ionization rate, and this should be compared with rate constants observed in the other cases. If internal return occurs in cases

(11) S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2171 (1952).

(12) S. Winstein, K. C. Schreiber and Richard Heck, unpublished work; S. Winstein, paper at Organic Reaction Mechanisms Symposium, American Chemical Society Meeting, New York, Sept. 7, 1951.

(13) S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2165 (1952).

TABLE IV

VARIATION OF SOLVOLYSIS RATES OF 2-ARYLETHYL p-TOLUENESULFONATES WITH SOLVENT AT 75°

		Rel. rates			Apparent	AcOH ΔH‡, kcal./mole	AcOH ΔS‡, e.u.	HCOOH ΔH‡, kcal./mole	HCOOH ΔS‡, e.u.
	Compound	EtOH	AcOH	HCOOH	m^a				
H	CH₃CH₂OTs	39	1	25	0.374	24.4	−16.7	22.1	−16.5
J	⟨benzene⟩—CH₂CH₂OTs	24.6	1	131	.570	24.9	−17.3		
K	⟨benzene, OCH₃⟩—CH₂CH₂OTs	1.2	1	254	.648	26.7	− 5.7		
L	CH₃O—⟨benzene⟩—CH₂CH₂OTs	1.6	1	212	.627	25.5	− 8.8	21.7	− 9.2

^{a} [log k_{HCOOH} − log k_{AcOH}]/3.713.

A, C and G, the titrimetric rate constant still measures total ionization rate because the rearranged esters would be so reactive that internal rearrangement would be included in the measured solvolysis rate.[11] Similarly, while it is not known to what extent internal return plays a part in solvolysis of E and F, the rearranged esters, such as XI from F,

XI
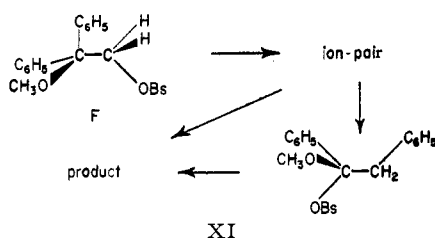
would be so reactive that the observed solvolysis rate constant measures total ionization rate.[14]

Although only crude corrections are used in deriving the values of "estimated k/k_c" in Table III, they suffice to show that, in the primary cases E and F, the magnitude of anchimeric assistance in the pinacol rearrangement reaches that in the Wagner–Meerwein rearrangement, a β-methoxyl group being nearly equivalent to a β-phenyl or two β-methyl groups. Thus we have the sequence of relative effectiveness of β-substituents other than the participating phenyl group: $\{[(C_6H_5)_2] \cong [(C_6H_5)(OCH_3)]\}$, 1.6–4 × 10⁶ > $\{[CH_3O] \cong [C_6H_5] \cong [(CH_3)_2]\}$, 2.5–3.5 × 10³ > [CH₃], 4 × 10².

The 2-Arylethyl Series.—The variation of rate with solvent and other aspects of the solvolysis of C₂H₅OTs, H,[9] C₆H₅CH₂CH₂OTs, J, 2-o-anisylethyl OTs, K and 2-p-anisylethyl OTs, L, are summarized in Table IV. The solvent change at 75° from acetic acid to formic acid produces a rate increase by a factor of 25 for H, 131 for J, and 254 and 212 for

(14) Even if internal return is important for F, phenyl participation still occurs in the rate-determining ionization to the ion-pair. Methoxyl participation and internal return would yield the ester XII

XII
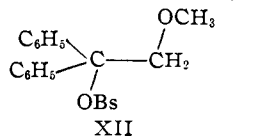
which would be expected⁴ to yield (C₆H₅)₂C—CH₂ and, to the extent pinacol rearrangement product is formed, (C₆H₅)₂CHCHO. The latter would be expected from XII just as it is obtained from 1,1-diphenylethylene glycol or its derivatives under conditions which ionize the tertiary C–O bond (see Experimental).

K and L, respectively, the factor in the case of the latter two resembling that for neopentyl.[9] These factors give rise to apparent values of m, which measure sensitivity of rate to ionizing power[6,15] and these values of m are listed in Table IV. For 2-p-anisylethyl OTs, L, just as for C₂H₅OTs, H,[9] the increase in rate attending the solvent change is due to a change in ΔH‡, the change in ΔS‡ being negligible.
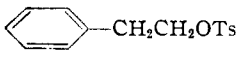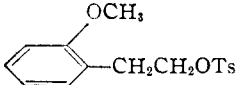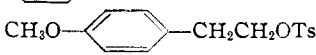
Inspection of the data makes it very probable that participation in the rate-determining step of solvolysis is serious in the case of 2-o-anisylethyl and 2-p-anisylethyl p-toluenesulfonates K and L, at least in acetic and formic acid solvents. The solvent rate sequences EtOH:AcOH:HCOOH for the different substances H–L, are interesting, the sequence being 39:1:25 for C₂H₅OTs, H; 25:1:131 for C₆H₅CH₂CH₂OTs, J; 1.2:1:254 for 2-o-anisylethyl OTs, K; and 1.6:1:212 for 2-p-anisylethyl OTs, L. Ethanol, a much more nucleophilic and only slightly less ionizing solvent[9,15] than acetic acid gives much higher rates than acetic acid with H and J but rates nearly equal to those in acetic acid with K and L. The solvolysis of the latter two substances is clearly very much less sensitive to nucleophilic character of the solvent. Also with respect to ΔS‡ in acetic acid, the solvolyses of K and L differ from those of H and J. For K and L, the values of ΔS‡ are similar and much higher than those for H and J.

The structural rate sequences shown in Table V are very helpful. In ethanol, where solvolysis is most apt to involve solvent participation (II) throughout the structural range, the sequence H:J:K:L is 1:0.24:0.28:0.45, all three 2-arylethyl esters, J, K and L, being slightly slower than the ethyl ester, H. In acetic acid the sequence is 1:0.37:8.9:10, 2-phenylethyl J being slower than ethyl H, but the 2-anisylethyls K and L being faster than ethyl H by a factor of ca. 10. Thus o-methoxyl and p-methoxyl enhance rate by factors of 24 and 27, respectively. In formic acid as solvent, the sequence is 1:2:93:94, even 2-phenylethyl being slightly faster than ethyl and the 2-anisylethyls being faster than ethyl by a factor of ca. 10². Thus p-methoxyl is rate-enhancing by a factor of 47, the factor being larger than for introduction of a p-methoxyl group into the benzylmethylcarbinyl ester.[16]

(15) E. Grunwald and S. Winstein, THIS JOURNAL, 70, 846 (1948).

(16) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, 74, 1140 (1952).

TABLE V

RELATIVE RATES OF 2-ARYLETHYL p-TOLUENESULFONATES
AT 75°

		Rel. k_{EtOH}	Rel. k_{AcOH}	Rel. k_{HCOOH}
H	CH₂CH₂OTs	1	1	1
J	⟨◯⟩—CH₂CH₂OTs	0.24	0.37	2.0
K	⟨◯⟩—CH₂CH₂OTs (OCH₃)	.28	8.9	93
L	CH₃O—⟨◯⟩—CH₂CH₂OTs	.45	10.0	94

The relative rates are most easily understood on the basis that there is anchimeric assistance to ionization of the 2-anisylethyl p-toluenesulfonates K and L in acetic and formic acids. While tracer techniques are required for further proof, it would appear in the case of 2-p-anisylethyl p-toluenesulfonate L that p-anisyl participation[16] (XIII) dominates the situation. The extent of anchimeric as-

XIII
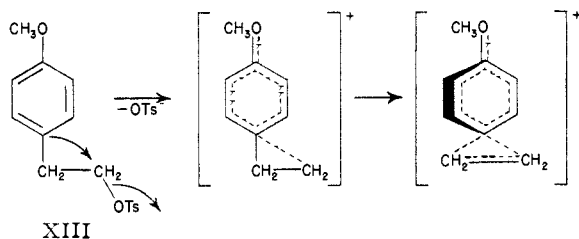
sistance may be estimated as before by comparison with neopentyl[2,9] A. The 2-p-anisylethyl ester L is *ca.* 100 times as reactive as neopentyl A in AcOH and HCOOH at 75°. If one makes the correction by which p-anisyl decreases k_c approximately the same as for phenyl (*e.g.*, p-methoxyphenylacetic acid is nearly as strong as phenylacetic acid) one derives an "estimated k/k_c" (as in Table III) of *ca.* 1000. On this crude basis, solvolysis of L is at least 10³ times as fast as solvolysis would be if it were of the Lim. variety[6] and anchimerically unassisted.

Other modes of anchimeric assistance are conceivable with the 2-anisylethyl esters K and L. One kind would involve hydrogen participation XIV, the anisyl group being a rate-enhancing but not a directly participating β-group.[2] This would give rise to 1-p-anisylethanol or p-methoxystyrene in the product, and we have shown that this could not be occurring to any serious extent.

XIV

XV   XVI
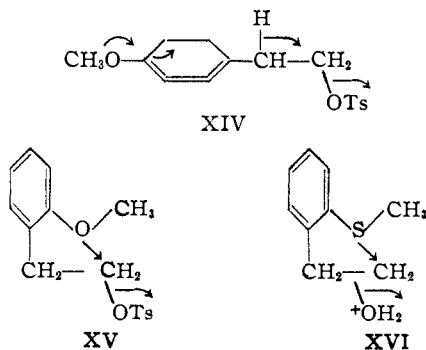
Another kind of assistance conceivable for the 2-o-anisylethyl p-toluenesulfonate K would involve direct participation by the o-methoxyl group as symbolized in XV, analogous to the participation of the methylthio group in the reaction of 2-o-methylthiophenylethanol with hydrogen bromide[17] (XVI). However, the close correspondence between the effects of the o-anisyl and p-anisyl groups on rate leaves no evidence that o-anisyl has a different function than p-anisyl (see XIII).
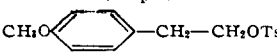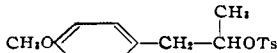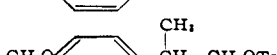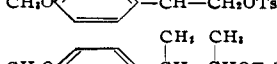
In the case of 2-phenylethyl p-toluenesulfonate (J) solvolysis, the relatively large rate increase attending the solvent change, AcOH → HCOOH, and the fact that J is twice as reactive as C₂H₅OTs (H) in formic acid suggests that phenyl participation in the rate-determining step may be prominent in formic acid.[18] It can be recalled that with benzylmethylcarbinyl derivatives,[16] phenyl participation is serious in formic acid and yet solvolysis rate is slightly less than for isopropyl. There are no clear indications from the kinetics that phenyl participation is very important in acetic acid, although the data would be consistent with some successful competition of phenyl with solvent participation.

Effect on Rate Due to α- and β-Methyl Groups.— The evidence that p-anisyl and phenyl participate in the rate-determining step of solvolysis of the ethyl system ($P_\beta P_\alpha^7$) makes it possible to scrutinize the dependence of rate of anchimerically assisted ionization on α- and β-methyl substitution. Table VI summarizes relative rates for the 2-p-anisylethyl series (XVII) and Table VII for the 2-phenylethyl series (XVIII). In writing down relative

XVII   XVIII
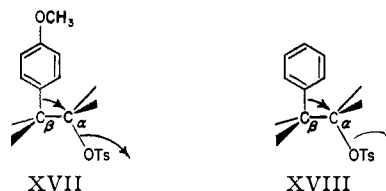
rates of ionization in Tables VI and VII, internal return[11,13] represents a complication. The procedure in choosing rate constants to compare for

TABLE VI

EFFECT OF α- AND β-METHYL GROUPS ON SOLVOLYSIS RATE
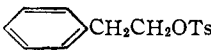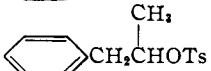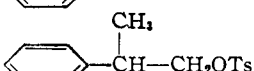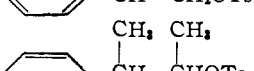OF 2-p-ANISYLETHYL p-TOLUENESULFONATE
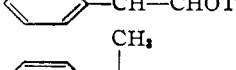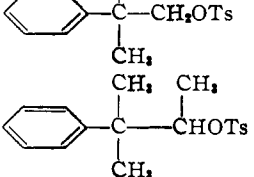
	Compound	No. of Me groups N_β	No. of Me groups N_α	AcOH, 49.7°— Rel.[a] k_{AcOH}	log k/k_0 obsd.	log k/k_0 calcd.
L	CH₃O⟨◯⟩—CH₂—CH₂OTs			1.0	0.0	0.0
M	CH₃O⟨◯⟩—CH₂—CHOTs[16] (CH₃)	1		27.7	1.44	1.44
N	CH₃O⟨◯⟩—CH—CH₂OTs[11] (CH₃)	1		15.2	1.18	1.18
P	CH₃O⟨◯⟩—CH—CHOTs[16] (CH₃ CH₃)	1	1	430	2.63	2.62

[a] Relative titrimetric rate constants, k_t, except in case N for which k_p was used.

(17) G. M. Bennett and M. M. Hafez, *J. Chem. Soc.*, 652 (1941).

(18) It is interesting that some phenyl migration occurs in nitrous acid deamination of C¹⁴-labeled 2-phenylethylamine [J. D. Roberts, Paper at Organic Reaction Mechanisms Symposium, American Chemical Society, New York, Sept. 7, 1951].

Table VII

Effect of α- and β-Methyl Groups on Solvolysis Rate of 2-Phenylethyl p-Toluenesulfonate

Compound	No. of Me groups N_β	N_α	HCOOH, 25.12° Rel.[a] k_{HCOOH}	log k/k0 obsd.	log k/k0 calcd.	AcOH, 49.7° Rel.[a] k_{AcOH}	log k/k0 obsd.	log k/k0 calcd.
J ⟨⟩CH₂CH₂OTs			1.0	0.0	0.0	0.22		
Q ⟨⟩CH₂CHOTs (CH₃)	1		76	1.88	1.95	8.0		
B ⟨⟩—CH—CH₂OTs (CH₃)	1		8.4	0.92	0.99	1.0	0.0	0.0
S ⟨⟩—CH—CHOTs (CH₃ CH₃)	1	1	1240	3.09	2.94	54.8	1.74	1.88
C ⟨⟩—C—CH₂OTs (CH₃ CH₃)	2					4.9	0.69	0.83
T ⟨⟩—C—CHOTs (CH₃ CH₃ CH₃)	2	1				1020	3.01	2.71

[a] For the relative rates, the following comparisons were used: Comparisons: T/C; C/S; S/B; B/Q; Q/J. Rate ratio: k_t/k_t; $k_t/k\alpha$; $k\alpha/(k_p + k_r)$; k_p/k_t; k_t/k_t.

each successive pair of compounds was to use total ionization rates, wherever possible. When the necessary data were not available for both members of a pair of compounds then the constants used for both materials were that part of the total ionization rate which did not result in return (e.g., k_p for N or k_t for P).

Examining first the 2-p-anisylethyl series (XVII, Table VI), it is seen that the introduction of an α-methyl group into 2-p-anisylethyl (L) increases ionization rate by a factor of 28, precisely the factor, previously commented on,[11] obtained on introduction of an α-methyl group into 2-p-anisyl-1-propyl (N). Similarly, the introduction of a β-methyl group into 2-p-anisylethyl (L) increases rate by a factor of 15.2, the same factor (15.5) previously[16] observed on introduction of a β-methyl group into p-methoxybenzylmethylcarbinyl (M).

The indications are that the effects on rate of α- and β-methyl groups are additive, a simple equation of the type (2) relating free energy of activation, $\Delta F_\Delta^{\ddagger}$, of the anchimerically assisted ionization to the number of α- and β-methyl groups, N_α and N_β, respectively. This is the equation previously[7] used in connection with participation by functional

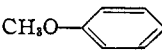$$\Delta F_\Delta^{\ddagger} = L_\Delta - d_\alpha N_\alpha - d_\beta N_\beta \qquad (2)$$

neighboring groups, L_Δ denoting free energy of activation of the unmethylated ethyl case and d_α and d_β being parameters for the stabilization of the transition state per α- or β-methyl group, respectively. Equation (2) is readily transformed to (3), where

$$2.303RT \log \frac{k}{k_0} = d_\alpha N_\alpha + d_\beta N_\beta \qquad (3)$$

k/k_0 is the rate of a compound (k) relative to the unmethylated ethyl case (k_0). The data in Table VI for the 2-p-anisylethyl series lead to $d_\alpha = 2.13$ and $d_\beta = 1.74$ kcal./mole (Table VIII) and these parameters reproduce the limited data well, as shown in Table VI.

For the 2-phenylethyl series in formic acid (Table VII), the structural range is the same as for the 2-p-anisylethyl series. Values of d_α and d_β of 2.68 and 1.36 are indicated (Table VIII) and, as shown in Table VII, these parameters in equation (3) reproduce log k/k0 to ±0.10 on the average. For the 2-phenylethyl series in acetic acid, data are available over the structural range up to $N_\alpha = 1$; $N_\beta = 2$ (Table VII). However, for the first two members of the series, J and Q,[16] the phenyl group has not yet taken over substantial control of the rate-determining step, as in the cases[3,11-13] B-T. Therefore equation (3) was applied to the four cases B, S, C and T, 2-phenyl-1-propyl[11] (B) being made the reference case. Table VIII lists the values 2.80 and 1.23 for d_α and d_β, respectively, and Table VII shows that these parameters reproduce the log k/k0 values to ±0.19 on the average.

Table VIII

Parameters for Rate Effects of Methyl Groups

Neighboring group	Solvent	Temp., °C	d_α, kcal./mole	d_β, kcal./mole
CH₃O—⟨⟩	AcOH	49.7	2.13	1.74
⟨⟩	HCOOH	25.12	2.68	1.36
⟨⟩	AcOH	49.7	2.80	1.23
I	AcOH	25	(3.2)[a,7]	1.79[7]
Br	AcOH	25	(3.2)[a,7]	1.79[7]
OH	H₂O–Dioxane	45	2.51[b]	
O⁻	H₂O	18	1.45[7]	1.67[7]

[a] Indirect values[7] by method which also required a choice for parameter for effect of α-methyl groups on k_0. [b] Assuming OH participation in ionization of isobutylene and trimethylethylene bromohydrins,[19] the α-methyl group enhances rate[19] by a factor of ca. 50.

The parameters are roughly of the same order of magnitude for neighboring anisyl and phenyl;

(19) C. M. Suter and H. D. Zook, This Journal, 66, 738 (1944).

d_α is smaller in the case of neighboring anisyl, which most probably indicates that the cationic character[7] of carbon atom C_α tends to be smaller in the transition state when the neighboring group is anisyl. It is interesting to compare the parameters with those for functional group participation[7] and this is done in Table VIII, where values are included for I, Br, OH and O⁻. The d_β values are all similar and, except for the O⁻ group, which represents a new charge-type, the values of d_α are not widely different.

Experimental Part

2-Methoxy-2-phenylethyl Benzenesulfonates.—Conversion of 2-methoxy-2-phenylethyl alcohol[4] to p-toluenesulfonate in the usual manner and recrystallization from petroleum ether yielded a material, m.p. 26°.

Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.75; H, 6.34. Found: C, 62.72; H, 5.92.

Analogously, the p-bromobenzenesulfonate, m.p. 59.5–60°, was prepared.

Anal. Calcd. for $C_{15}H_{15}O_4SBr$: C, 48.52; H, 4.07. Found: C, 48.55; H, 4.29.

2,2-Diphenyl-2-methoxyethanol.—A mixture of 50 g. (0.219 mole) of benzilic acid and 0.407 mole of phosphorus pentabromide was heated with stirring for an hour on a water-bath. When the mixture changed to a liquid, it was poured into ice-water with vigorous stirring. The resulting solid was filtered, washed with water, dried on a clay plate, and added slowly to 348 ml. of anhydrous methanol, the solution being allowed to stand overnight. Water was added, the product was taken up in ether and the ether solution was dried over anhydrous potassium carbonate. Distillation at reduced pressure yielded 39.3 g. (70.0%) of methyl 2,2-diphenyl-2-methoxyacetate, b.p. 176.3–178.0° (10.8 mm.) [reported[8] b.p. 191.2° (19 mm.)].

A 39.0-g. (0.15 mole) quantity of methyl 2,2-diphenyl-2-methoxyacetate was added slowly to a 3.6-g. (0.090 mole) quantity of lithium aluminum hydride in 105 ml. of purified dioxane. The rate of addition was adjusted so that the heat of reaction kept the solution warm, and the solution was heated below reflux for an hour following the addition. The reaction mixture was worked up in the usual way with water and 10% sulfuric acid. The ether extract, after drying over anhydrous potassium carbonate, was concentrated, and to the residue was added 150 ml. of ethanol and 150 ml. of 2 N potassium hydroxide. The resulting mixture was refluxed for an hour, extracted with ether and the ether solution dried over anhydrous potassium carbonate. Distillation of the ether and recrystallization yielded 19.66 g. (0.086 mole), 57.3%, of 2,2-diphenyl-2-methoxyethanol, m.p. 87.4–89.9°, m.p. 89.6–90.2° after another recrystallization.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.84; H, 7.31.

2,2-Diphenyl-2-methoxyethyl p-Bromobenzenesulfonate.—Conversion of the corresponding alcohol to the bromobenzenesulfonate in the usual manner gave, in 89% yield, material, m.p. 122.3–123.7°, m.p. 122.6–123.3° after another recrystallization.

Anal. Calcd. for $C_{21}H_{19}O_4SBr$: C, 56.38; H, 4.28. Found: C, 56.10; H, 4.32.

Solvolysis of 2,2-Diphenyl-2-methoxyethyl Bromobenzenesulfonate.—A solution of 8.94 g. (0.020 mole) of ester and 2.16 g. (0.022 mole) of potassium acetate in 400 ml. of 80% aqueous dioxane was held at 75° for 95 hours. The solution was poured into 800 ml. of water and extracted with ether, the ether extract being dried over anhydrous potassium carbonate. The ether was distilled off through a 13-inch Vigreux column and the remaining dioxane was removed at reduced pressure (water aspirator) to leave 3.40 g., 89%, of solid residue, m.p. 48.5–50.5°, mixed m.p. with desoxybenzoin (Eastman Kodak Co. White Label recrystallized material, m.p. 54.3–55.2°) 49.5–53.8°. Recrystallization from water–ethanol solution gave 2.67 g. of material, m.p. 52.0–54.2°, mixed m.p. with desoxybenzoin 51.5–54.5°. A second recrystallization from pet. ether gave 2.05 g. of solid material, m.p. 54.0–54.5°, mixed m.p. with desoxy-

benzoin 53.9–55.2° (reported[20] for desoxybenzoin recrystallized from methanol, m.p. 55–56°).

Treatment of 2,2-Diphenyl-2-methoxyethanol with Aqueous Sulfuric Acid.—A solution of 0.74 g. (0.00148 mole) of 2,2-diphenyl-2-methoxyethanol in 15 ml. of aqueous 20% sulfuric acid was refluxed for 4.5 hours. The cooled solution was extracted with ether, and the ether extract was washed with 5% aqueous sodium bicarbonate solution. After drying the ether extract over anhydrous potassium carbonate, the ether was distilled off through a 35-cm. centered rod column and the semicarbazone derivative of the residue was prepared by adding 10 ml. of ethanol, 1 g. of semicarbazide hydrochloride and 1 g. of sodium acetate. The solution was shaken, placed in a beaker of boiling water and allowed to cool until a solid crystallized out. After filtration and washing, 0.53 g., 68%, of a solid, m.p. 142.7–153.9°, was obtained. Two recrystallizations from ethanol raised the m.p. to 159.0–160.6°, mixed m.p. with desoxybenzoin semicarbazone (m.p. 146.8–148.2°) 105.3–132.7° (reported for diphenylacetaldehyde semicarbazone by Stoermer and co-workers[21] m.p. 160°, and by Tiffeneau[22] m.p. 162°).

2-Phenylethyl p-Toluenesulfonate.—This material, m.p. 35.5–36.6°, was prepared in the usual manner in 63% yield from purified 2-phenylethanol.

Anal. Calcd. for $C_{15}H_{16}SO_3$: C, 65.19; H, 5.84. Found: C, 65.07, H, 6.01.

2-o-Methoxyphenylethyl p-Toluenesulfonate.—2-o-Methoxyphenylethanol was prepared from purified o-bromoanisole and ethylene oxide via the Grignard reagent; b.p. 133–135° (10 mm.) [reported[23,24] 133–135° (14 mm.), 136° (12 mm.)]. The toluenesulfonate, m.p. 55.5–56.0° (reported[22] m.p. 56–57°), was prepared in the usual fashion in 49.1% yield.

Anal. Calcd. for $C_{16}H_{18}SO_4$: C, 62.72; H, 5.92. Found: C, 62.74; H, 5.99.

2-p-Methoxyphenylethyl p-Toluenesulfonate.—2-p-Methoxyphenylethanol was prepared from the Grignard reagent of p-bromoanisole and ethylene oxide.[25] Distillation yielded material, b.p. 139–141° (10 mm.) [reported 145–160° (10 mm.),[25] 140–145° (12 mm.)].[26] The alcohol was obtained as a crystalline solid, m.p. 27–28° (reported[27] 28°), b.p. 130–132° (6.5 mm.), by several crystallizations and distillations. The toluenesulfonate, m.p. 57–58°, was prepared in the usual manner.

Anal. Calcd. for $C_{16}H_{18}SO_4$: C, 62.72; H, 5.92. Found: C, 62.61; H, 6.03.

1-p-Methoxyphenylethanol.—This material was prepared from the Grignard reagent of p-bromoanisole and acetaldehyde. The bulk of the product distilled at 95–95.5° (1.0 mm.), displayed $n^{25.5}$D 1.5349–1.5354, and gave a very slow test with bromine in carbon tetrachloride. A fraction, b.p. 95.0° (1.0 mm.), $n^{25.5}$D 1.5350, was employed for determination of the infrared spectrum.

Formolysis of 2-p-Methoxyphenylethyl p-Toluenesulfonate.—Into a one-liter flask were placed 27.0 g. (0.088 mole) of the ester, 7.0 g. (0.089 mole) of dried sodium formate and 880 ml. of dry formic acid (0.04% water). The flask was placed in a 50° bath for 15 hours (11.5 half-lives). The formic acid solution was diluted with one liter of ice-water and extracted with three 500-ml. portions of pet. ether (b.p. 30–52°). The pet. ether extracts were washed with 250 ml. of water, two 250-ml. portions of 5% sodium bicarbonate solution, and finally with 250 ml. of water. After drying with anhydrous potassium carbonate, the pet. ether was removed through an efficient column leaving an oil. This oil was reduced with 7.6 g. (0.20 mole) of lithium aluminum hydride (in ether) to give 9.0 g. (0.059 mole, 67%)

(20) C. F. H. Allen and W. E. Barker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 156–157.

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(25) F. B. LaForge and W. F. Barthel, J. Org. Chem., **9**, 250 (1944).

(26) A. Horeau and J. Jacques, Bull. soc. chim., [5] **13**, 382 (1946).

(27) G. Levy, Ann. chim., **9**, 5 (1938).

of crude alcohol. Distillation of the crude product through a short Vigreux column yielded 7.3 g. (0.048 mole, 54.6%) of pure alcohol, b.p. 120–125° (5 mm.), m.p. 27–28°, and 1.0 g. of residue, a light brown oil. Tests of the crude product and purified alcohol with aqueous potassium permanganate (2% in water) and ferric chloride solution were negative.

Rate Measurements.—Dry acetic acid,[5,28] absolute ethanol, 0.05% water, and dry formic acid,[9] b.p. 30–31° (50 mm.), 0.01–0.18% water by Karl Fischer titration, were

(28) S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, 70, 812 (1948).

employed. Aqueous dioxane, 80.78% dioxane by volume, was prepared by addition of purified dioxane, freshly distilled from sodium, to 20 volumes of water up to a total of 100 volumes of solution.

The methods employed for the rate measurements were essentially those previously employed.[5,6,9] Titration of aliquots in the ethanolyses was carried out with standard sodium methylate in methanol using the mixed indicator, methyl red and brom cresol green. For the solvolyses in aqueous dioxane, aliquots were titrated with standard aqueous base to the phenolphthalein end-point.

LOS ANGELES 24, CALIFORNIA

Neighboring Carbon and Hydrogen. XV. Rearrangement as a Sequel to Neighboring Functional Group Participation. Solvolysis of 2-Methyl-2-methoxy-1-propyl p-Bromobenzenesulfonate

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An exploratory study of the solvolysis of 2-methyl-2-methoxy-1-propyl p-bromobenzenesulfonate has shown isobutyraldehyde to be the chief product. The rate of solvolysis is relatively high, methoxyl participation in the rate-determining ionization step supplying a substantial driving force. Glycol monomethyl ether or vinyl ether are not intermediates for isobutyraldehyde formation, the present case illustrating pinacol type rearrangement by a chain of steps commencing with functional neighboring group participation.

It is possible for the pinacol type rearrangement to be associated with a sequence of events beginning with neighboring functional group participation, and we deal in the present article with an instructive case in point. This case is the solvolysis of 2-methyl-2-methoxy-1-propyl p-bromobenzenesulfonate (IV) which gives rise, at least largely, to isobutyraldehyde. An exploratory study of this solvolysis is the subject of this manuscript.

The bromobenzenesulfonate IV required for study was prepared from the corresponding alcohol III, this being available from the opening of isobutylene oxide with methanol under acidic conditions.[1] The isomeric alcohol I was prepared by the opening of isobutylene oxide with methanol under basic conditions analogous to the opening of trimethylethylene oxide.[2]

In spite of the high hindrance to nucleophilic attack on C_α by external reagents, the bromobenzenesulfonate IV was quite reactive in solvolysis, which disclosed at the very outset that some kind of anchimeric[3] assistance is involved in the rate-determining ionization step. The solvolysis rate constants of IV in glacial acetic acid and in the solvent used for product isolation, 80% dioxane, are given in Table I. The value of the rate constant in acetic acid, corrected by a factor[4] of 3 to bring the value down to that for the corresponding toluenesulfonate, relative to the value for neopentyl toluenesulfonate[4] gives the comparison which shows that the bromobenzenesulfonate IV is fifteen times as reactive in solvolysis as the

(1) K. R. Edlund, U. S. Patent 1,968,032, July 31, 1934.

(2) (a) S. Winstein and L. L. Ingraham, THIS JOURNAL, 74, 1160 (1952); (b) S. Winstein and R. B. Henderson, "Ethylene and Trimethylene Oxides," in Elderfield, "Heterocyclic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950.

(3) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, 75, 147 (1953).

(4) S. Winstein, et al., ibid., 74, 1113 (1952).

TABLE I

RATE CONSTANTS FOR REACTION OF 2-METHOXY-2-METHYL-1-PROPYL p-BROMOBENZENESULFONATE (IV)

Solvent	Concn., M	Other solute	Temp., °C.	k, sec.$^{-1}$
AcOH	0.047		74.73	$(3.55 \pm 0.08) \times 10^{-6}$
"80%" dioxane	.051	0.0587 M KOAc	99.73	$(3.89 \pm 0.08) \times 10^{-5}$

neopentyl ester. If one allows for the fact that a β-methoxyl group would, in the absence of participation, reduce an ionization rate by a factor of
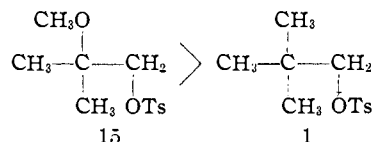
approximately[5] 10^2, it becomes clear that bromobenzenesulfonate IV ionizes at a rate at least 1500 times that which would prevail if no anchimeric assistance were involved. The value of 1500 represents a lower limit to the driving force due to participation in the rate-determining ionization step if neopentyl toluenesulfonate already has an enhanced rate due to carbon participation.[6] Of the two possible participations to be considered, namely, that due to the neighboring methoxyl group (IV) or that due to the neighboring methyl group (XV), the latter can be ruled out immediately on the basis of the final products. Methyl participation (XV) would result in methyl ethyl ketone as a product and, since the product is very largely isobutyraldehyde, methoxyl participation (IV) is therefore indicated. The large driving force associated with methoxyl participation in the bromobenzenesulfonate IV supports the previous

(5) S. Winstein, E. Grunwald and L. Ingraham, ibid., 70, 821 (1948).

(6) S. Winstein and H. Marshall, ibid., 74, 1120 (1952).