Phenyl vs. Methyl Migration Aptitudes in Some Carbonium Ion Reactions of Neophyl Derivatives[1]

By William H. Saunders, Jr., and Robert H. Paine

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Solvolyses of neophyl chloride, tosylate and brosylate in formic acid and neophyl tosylate in acetic acid were performed. The product olefins and esters were examined by gas chromatography. The presence of material having a carbon skeleton corresponding to methyl migration was unequivocally established. This constituted 0.05% of the total product in formolysis of the chloride, 0.3% in acetolysis of the tosylate and 0.7% in formolysis of the tosylate. The reaction conditions were shown not to cause any carbon-skeleton rearrangements of the products. The dehydration of neophyl alcohol by sulfuric acid was examined briefly. Partial rate factors were computed for phenyl and methyl migration in the acetolysis and tentative conclusions drawn concerning the nature of the transition state for methyl migration.

Of the many studies of migration aptitudes in the literature,[2] the majority deal with competition between different aryl groups. Less is known about alkyl vs. alkyl, and still less about alkyl vs. aryl.

Most available data agree on a qualitatively high aryl/alkyl ratio. For example, Cram detected no methyl migration in solvolyses of 3-phenyl-2-butyl derivatives[3] and Winstein found only products of phenyl migration in the acetolysis of neophyl brosylate.[4] Considerable methyl migration was noted in the deamination of 3-phenyl-2-butylamine,[5] but deaminations often differ markedly from other carbonium ion reactions. The only other examples of alkyl competing successfully with aryl are in migrations to oxygen.[6]

With this background, a careful investigation of some typical carbonium ion reactions, solvolyses of neophyl derivatives, was undertaken to determine whether methyl migration was detectable in a simple system. Conditions and rates of solvolysis in this system have been investigated before.[4,7] The possible products of carbonium ion reactions of neophyl derivatives are shown in Fig. 1.

The plan was to use gas chromatography in an effort to analyze for the probably minor quantities of methyl-migrated products. We hoped to simplify analysis of the olefinic fraction by hydrogenation to a mixture of the saturated hydrocarbons sec-butylbenzene and isobutylbenzene. Unfortunately, we could find no conditions or column materials which enabled the separation of these substances by gas chromatography.

Attention was then turned to the preparation of reference samples of the various olefins. These were obtained unambiguously, though usually in poor yield, by the Wittig reaction.[8] The phos-

phonium salt and ketone used in each case were: for IV, benzyltriphenylphosphonium bromide and acetone; for V, methyltriphenylphosphonium bromide and phenylacetone; for VI, methyltriphenylphosphonium bromide and propiophenone; and for VII, ethyltriphenylphosphonium bromide and acetophenone.[9]

Comparison samples of the rearranged alcohols were also needed; II was available commercially. The reaction of ethylmagnesium bromide with acetophenone gave III. The product of phenyl plus hydride migration, VIII, was also present in the reaction mixture and an authentic sample was obtained by reduction of isobutyrophenone.

The solvolyses given careful study were formolysis of neophyl chloride, tosylate and brosylate, and acetolysis of neophyl tosylate. Reaction conditions and product compositions are reported in Table I. The identity of VIIa was positively established in one run by the isolation of a small amount of nearly pure VIIa from several passes through the gas chromatograph. The infrared spectrum showed clearly that this was VIIa along with a little IV. All solvolyses were performed in the presence of at least an equivalent of the conjugate base of the solvent to minimize any possible acid-promoted isomerization.

Runs 32–35 show that the products are not entirely stable to the reaction conditions. There is some double-bond position isomerization in both formic and acetic acids, though more in the former. The phenyl-migrated olefins undergo partial addition of solvent to given esters. Interestingly, the methyl-migrated olefins do not, which probably explains the complete absence of methyl-migrated ester from all the reaction mixtures. The product compositions are obviously not entirely the result of kinetic control. No carbon-skeleton isomerization is detectable, however, so the methyl-migrated material VIIa must be a primary product of the reaction.

The distribution of double-bond position isomers is as expected. The conjugated isomer IV predominates over the unconjugated V by 5:1 in acetolysis and up to 70:1 in formolysis. The variability of the IV/V ratio in formolysis is probably ascribable to unequal rates of reaction of IV and V with the solvent. The apparent absence of any methyl-migrated product except for VIIa is not unex-

(1) This work was supported in part by the Office of Ordnance Research, U. S. Army. R. H. Paine received a stipend during the Summer of 1957 from the Hercules Powder Co. Grant.

(2) For reviews, see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. 9; (b) D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 264 et seq.; (c) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 494 et seq.

(3) D. J. Cram, J. Am. Chem. Soc., 74, 2137 (1952).

(4) R. Heck and S. Winstein, ibid., 79, 3432 (1957).

(5) D. J. Cram and J. E. McCarty, ibid., 79, 2866 (1957).

(6) M. F. Hawthorne, W. D. Emmons and K. S. McCallum, ibid., 80, 6393 (1958).

(7) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, ibid., 74, 1113 (1952); (b) A. H. Fainberg and S. Winstein, ibid., 78, 2763 (1956); (c) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, ibid., 75, 147 (1953).

(8) G. Wittig and U. Schollkopf, Chem. Ber., 87, 1318 (1954).

(9) In Fig. 1, cis refers to the isomer having both methyl groups on the same side of the double bond. The ratio of VIIa to VIIb in the product of the Wittig reaction was about 4:1.

TABLE I

REARRANGEMENT REACTIONS OF NEOPHYL DERIVATIVES

Run	Reactant, concn.[a]	Solvent[b]	Other reagent, concn.	Reaction time, hr.	IV	V[d]	VIIa	II[e]	VIII[e]	Other
11	Ia, 2.6	HCO₂H	HCO₂Na, 2.6	18	76	9.1	0.05	7.9[g]	2.7[g]	C₆H₅CHO, 4.2
12	Ia, 2.6	HCO₂H	HCO₂Na, 2.6	41	94.8	4.5	0.07	f	f	C₆H₅CHO, 0.6
16	Ia, 0.27	HCO₂H	HCO₂Na, 0.27	24	93.5	5.1	Tr.	f	f	C₆H₅CHO, 1.1
17	Ia, .27	HCO₂H	HCO₂Na, .27	48	93.0	4.8	Tr.	f	f	C₆H₅CHO, 2.1
18	Ib, .27	HCO₂H	HCO₂Na, .27	22	59.4	5.2	0.69	29.4[g]	5.3	....
19	Ic, .27	HCO₂H	HCO₂Na, .27	43	66.6	2.1	.20	26.5[g]	4.4	....
20	Ib, .27	HCO₂H	HCO₂Na, .27	41	61.8	4.5	.62	30.1	2.7	....
21	Ib, .27	HCO₂H	HCO₂Na, .33	48	73.8	1.1	.77	20.6	4.4	....
22	Ic, .27	HCO₂H	HCO₂Na, .29	13	63.3	2.3	1.06	27.7	4.3	h
23	Ic, .27	HCO₂H	HCO₂Na, .29	20	63.7	1.2	0.17	30.2	4.6	VI, tr.
24	Ib, .22	HOAc	NaOAc, .24	24	78.1	16.0	0.29	5.0	0.6	....
29	Id	e	H₂SO₄	0.8	3.4	5.0	37.0	49.6	..	VI, 4.8[k]
30	Id	e	H₂SO₄	2.0	46.2	8.8	22.3	8.5	..	VI, 14.2[l]
31	Ic, 0.27	HCO₂H	HCO₂Na, 0.30	38	71.1	1.9	Tr.	23.2	2.9	....
32	IV	HCO₂H	HCO₂Na	39	73.8	..	..	20.7	5.4	....
33	i	HOAc	NaOAc	35	81.9	13.3	..	4.6	0.2	....
35	j	HCO₂H	HCO₂Na	39	..	..	75.3	..	..	VIIB, 17.8 VI, 6.9

[a] Concn. means moles of reactant per liter of solvent. [b] Reactions carried out at reflux temperature of solvent except in runs 29 and 30. [c] Id, 0.017 mole, and sulfuric acid, 0.042 mole, were mixed in 35 ml. of petroleum ether at 0–5°. [d] This represents V plus VIIb, if any, since these two were not resolved in the gas chromatograms. [e] These were determined as the alcohols after saponification (methanol and sodium methoxide) or reduction (lithium aluminum hydride) of the initial product mixture. Exceptions are noted. [f] Present but not analyzed for. [g] Mixture of formate and alcohol. [h] Over 90% of product became viscous and non-volatile (presumably polymeric) on standing. [i] Mixture of 88.3% IV and 11.7% V. [j] Mixture of 99.7% VIIa and 0.3% VIIb. [k] 90% of neophyl alcohol recovered. [l] 65% of neophyl alcohol recovered.

pected. The less-stable isomer VIIb would be covered by V in the gas chromatogram, and the least-stable isomer VI probably occurs in quantities below the limits of detection (though in one case, run 23, a trace peak corresponding to VI was observed). Our acetolysis product does differ somewhat from that reported by Heck and Winstein.[4] They obtained 60% olefin, of which only half was conjugated (ultraviolet spectrum) and 31% alcohol, nearly all of which was II. Their reaction was run at 75° rather than reflux, however, and probably involved less (if any) further reaction of initial products.

The most interesting aspect of our results is the demonstration that appreciable methyl migration occurs. After correction for the presence of two methyl groups, the phenyl/methyl migration aptitudes are 1.00:0.0035 for formolysis and 1.00: 0.0015 for acetolysis of the tosylate, and 1.00: 0.0003 for formolysis of the chloride. Formolysis of the brosylate gives results similar to those with the tosylate, but more scattered.[10]

The order of these migration aptitudes is as expected. Formolysis is generally a faster reaction with lower activation energy than acetolysis.[11] Less discrimination among the possible reaction paths is expected for formolysis and therefore more methyl migration. A similar argument applies to chloride vs. tosylate in formolysis. The tosylate is much more reactive[4,11] and again should give more methyl migration.

Data for rates of acetolysis of neopentyl and neophyl tosylates are available[7b] and, in combination with our results, permit the calculation of

partial rate factors for methyl migration. For neophyl tosylate at 99.58°, p_{CH_3} is 3.7 × 10⁻⁷ sec.⁻¹ and for neopentyl tosylate p_{CH_3} is 5.3 × 10⁻⁷ (one-third of the over-all rate constant).[12]
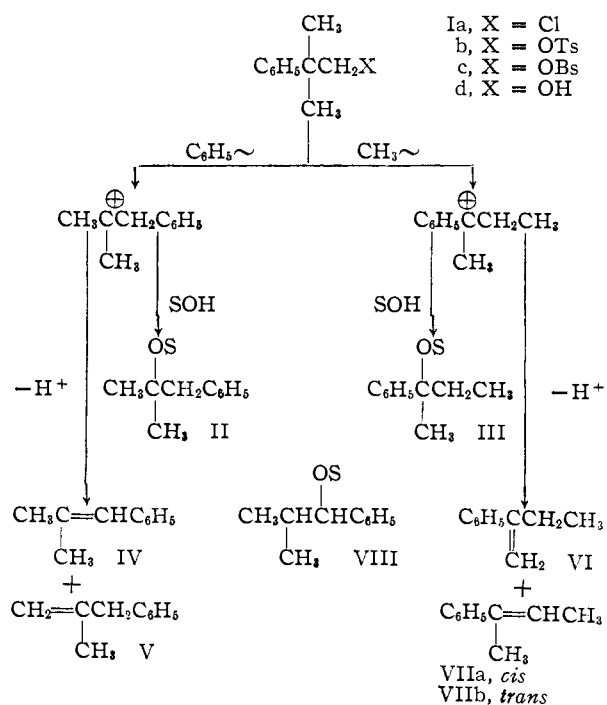

Fig. 1.—Possible products of the solvolysis of neophyl derivatives.

(10) For unknown reasons, the products from the brosylate were rather unstable and difficult to analyze; see footnote h, Table I.

(11) A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 79, 1608 (1957).

(12) Our calculation makes the reasonable assumption that methyl migration occurs in the rate-determining step of the acetolysis. In addition, the migration aptitudes were determined at reflux temperature rather than at 99.58°, but should not vary much with temperature.

The similarity of the two partial rate factors leads to the conclusion that methyl migrates at least as well from a carbon bearing two other methyls as from a carbon bearing a methyl and a phenyl. Any appreciable positive charge on the β-carbon would be much more effectively stabilized by phenyl. The transition state thus appears to have the methyl group still quite close to the β-carbon and to resemble the ground state much more than it does any possible bridged intermediate.

A brief investigation of the action of sulfuric acid on neophyl alcohol was prompted by Mosher's recent work.[13] He reports that distillation of neophyl alcohol from catalytic quantities of sulfuric acid gives mainly phenyl-migrated, but some methyl-migrated, product. We hoped that lower temperatures might give a kinetically-controlled product mixture, but the wide differences in product composition between two runs that differ only in time of reaction (Table I, runs 29 and 30) suggest that this goal was not achieved. The large proportion of methyl-migrated material may therefore arise simply from relative stabilities of the various products.

Experimental[14]

Neophyl chloride was prepared by adding methallyl chloride to a cold mixture of benzene and sulfuric acid.[15,16] Yields of 42–46% of material having b.p. 74–75° (3 mm.), n^{20}D 1.5255 resulted (lit.[16] b.p. 97–98° (10 mm.), n^{20}D 1.5250.)

Neophyl alcohol was obtained by oxidation of the Grignard reagent of neophyl chloride.[15] Our alcohol was contaminated with neophyl chloride and therefore was purified via the 3-nitrophthalate esters.[17] The two esters isolated (presumably corresponding to esterification at the two non-equivalent carboxyl groups) had m.p. 120–120.5° (Anal. C, 63.27; H, 5.02) and 152–153° (Anal. C, 63.14; H, 5.20. Calcd. for $C_{18}H_{17}O_6N$: C, 62.97; H, 4.99). Saponification of both esters yielded neophyl alcohol of b.p. 90–91° (3 mm.), n^{25}D 1.5222 (lit.[15] b.p. 131° (30 mm.), n^{20}D 1.5261).

Sulfonate Esters of Neophyl Alcohol.—The p-toluenesulfonate was prepared essentially in the manner of Tipson[18] and on recrystallization from ether–petroleum ether had m.p. 73.5–74.5° (lit.[7a] 74–75°). The same procedure using p-bromobenzensulfonyl chloride gave a product of m.p. 82.5–83.2° (lit.[7b] 80.8–81.5°).

Preparation of reference olefins was accomplished by the Wittig reaction.[8] A solution of butyllithium (ca. 0.2 mole) in ether was prepared,[19] its concentration determined, and an equivalent amount of the appropriate alkyltriphenylphosphonium halide added in small portions. The mixture was refluxed for 5 hours and an equivalent amount of the appropriate ketone added dropwise. Refluxing was continued for 4 hours, after which the triphenylphosphine oxide was removed by filtration and the ether solution washed with water and dried over magnesium sulfate. The ether was evaporated and the residual oil chromatographed on alumina using petroleum ether (b.p. 30–60°) as eluent. Some ketone which was not removed by chromatography or distillation remained in most cases and final purification was accomplished by gas chromatography. Since only samples for gas chromatographic comparisons were needed, there was

no attempt to obtain maximum yields. The yields were usually rather poor (10–20%).

Reactants and products were as follows: benzyltriphenylphosphonium bromide and acetone, 1-phenyl-2-methylpropene; methyltriphenylphosphonium bromide and propiophenone, 2-phenyl - 1 - butene; methyltriphenylphosphonium bromide and phenylacetone, 3-phenyl-2-methylpropene; ethyltriphenylphosphonium bromide and acetophenone, cis- and trans-2-phenyl-2-butene (these isomers were easily separated by gas chromatography).

Reference Alcohols.—2-Methyl-1-phenyl-2-propanol was commercially available (Eastman Kodak Co.) and was purified by distillation and gas chromatography.

2-Methyl-1-phenyl-1-propanol resulted from the treatment of isobutyrophenone (0.2 mole) with aluminum isopropoxide (0.1 mole) in refluxing isopropyl alcohol (300 ml.) for 4 hours. The product still contained some unreduced ketone which was removed by gas chromatography.

2-Phenyl-2-butanol resulted from the addition of ethylmagnesium bromide to acetophenone. The Grignard complex was decomposed with a cold saturated ammonium chloride solution and the product worked up as usual. Final purification was again accomplished by gas chromatography.

Reference Alkylbenzenes.—Isobutylbenzene was obtained from K. and K. Co. and sec-butylbenzene from Aldrich Chemical Co. Both were purified by distillation and gas chromatography.

Solvolyses of Neophyl Derivatives.—Anhydrous formic acid was obtained by stirring 98% formic acid with boric anhydride (10% by weight) followed by distillation.[20] Sodium formate and sodium acetate were Baker reagent grade dried over phosphorus pentoxide in a vacuum desiccator. Glacial acetic acid was stirred with acetic anhydride (10% by weight) for 24 hours and distilled.[21]

The neophyl derivative was dissolved in acetic acid containing a slight excess of sodium acetate, or in formic acid containing a slight excess of sodium formate and the mixture refluxed for the specified period of time. Solutions in acetic acid were homogeneous throughout the reaction. Reactions in formic acid either were heterogeneous from the outset (neophyl chloride) or became heterogeneous later (neophyl arylsulfonates). Specific reaction conditions and times are recorded in Table I.

The cooled reaction mixtures were extracted several times with petroleum ether (b.p. 30–49°) and the extracts washed with 3 M sodium carbonate until the washings were basic to litmus. The extracts were then washed with water and dried successively over magnesium sulfate and Drierite. The solvent was removed and the residue either submitted directly to gas chromatography or, usually, treated first with lithium aluminum hydride in ether or sodium methoxide in methanol to convert the ester portion of the product to alcohols. Results of the gas-chromatographic analyses are given in Table I. Some difficulty with autoxidation of the olefins was encountered in early runs (11, 12, 16, 17), but expeditious handling of the products almost completely eliminated this problem.

Reaction of Neophyl Alcohol and Sulfuric Acid.—To a mixture of concentrated sulfuric acid and petroleum ether (b.p. 30–49°) at 0–5° was slowly added a solution of neophyl alcohol in petroleum ether. The mixture was stirred 1–2 hours and neutralized at 0–5° with 3 M sodium carbonate. More petroleum ether was added and the organic layer separated and dried as in the solvolyses above. The residue after removal of the solvent was analyzed by gas chromatography (Table I).

Effects of Reaction Conditions on Products.—A sample of 2-methyl-1-phenylpropene (0.0084 mole) was refluxed for 39 hours with 1.26 moles of formic acid containing 0.02 mole of sodium formate. The reaction mixture was worked up as described above for the solvolyses of neophyl derivatives. No carbon-skeleton isomerization occurred as shown by gas chromatography (Table I, run 32).

cis-2-Phenyl-2-butene containing 0.29% of the trans isomer (total 0.02 mole) was refluxed for 39 hours with 4.0 moles of formic acid containing 0.04 mole of sodium formate. The work-up was as usual, but no formate esters were found in the product so the treatment with lithium aluminum hydride

(13) W. A. Mosher, Abstracts of 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(14) Melting points and boiling points are uncorrected.

(15) F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., J. Am. Chem. Soc., 65, 1469 (1943).

(16) W. T. Smith, Jr., and J. T. Stellas, Org. Syntheses, 32, 90 (1952).

(17) D. J. Cram, J. Am. Chem. Soc., 71, 3869, 3883 (1949).

(18) R. S. Tipson, J. Org. Chem., 9, 235 (1944).

(19) H. Gilman and J. W. Morton, Jr., in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1954, Vol. VIII, Chap. 6.

(20) S. Winstein and H. Marshall, J. Am. Chem. Soc., 74, 1120 (1952).

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

was omitted. Results of gas chromatographic analysis are given in Table I, run 35.

A mixture of 88.3% 2-methyl-1-phenylpropene and 11.7% 2-methyl-3-phenylpropene (total 0.013 mole) was refluxed for 35 hours with 2 moles of acetic acid containing 0.02 mole of sodium acetate. After the usual work-up, the product was analyzed by gas chromatography (Table I, run 33).

Gas Chromatographic studies were carried out on two instruments: Aerograph model A-90-C and Aerograph model A-110-C (Wilkins Instrument and Research, Inc.). Chromosorb (Johns–Manville, Inc.) was the stationary phase on all columns. Most of the work was done on two columns: $10' \times {}^{3}/_{8}''$ Carbowax 20M (Union Carbide Co.—a polyethylene glycol having a molecular weight of about 20,000) and $10' \times {}^{1}/_{4}''$ Ucon Polar (Wilkins Instrument and Research, Inc.—a polypropylene glycol of unstated molecular weight). Approximate operating conditions for the Carbowax 20M column were 200 ml. He/min. at a column temperature of 120° and for the Ucon column 60 ml. He/min. at 160°.

Good separations of the olefins from each other and from the alcohols were obtained, except for the failure to separate V and VIIb. Attempts to separate sec-butylbenzene and isobutylbenzene with a wide variety of column materials failed.

Analysis for the small amounts of VIIa required special

techniques. Except with large samples, VIIa appeared as a slope change on the tailing end of IV. Therefore a large (1.5–2.0 ml.) sample was introduced and the olefins and alcohols collected separately. Re-introduction of the olefins at a higher injector temperature usually gave essentially complete resolution of IV and VIIa. In one run enough VIIa was collected for an infrared spectrum. The sample was shown, by comparison with authentic samples, to be mainly VIIa, with some IV as the only detectable contaminant.

Under the usual conditions of the gas chromatographic analyses, neophyl chloride partially decomposes in the injector block to hydrogen chloride and rearranged olefins. Consequently, the products from neophyl chloride solvolyses were run through the gas chromatograph at lower injector temperatures to remove unreacted neophyl chloride (usually about 30% of the total product). The olefin fraction was then resubmitted with the injector at its usual temperature (about 50° above the column).

When reaction products containing formate esters were introduced without prior conversion of the esters to alcohols, partial decomposition to olefin and alcohol occurred (Table I, runs 11,18, 19). That this occurred in the gas chromatograph was shown by submission of pure ester, which still gave olefin and alcohol peaks. The alcohols were stable under the conditions adopted for the analyses.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. XVII.[1] Induced Common Ion Rate Depression and the Mechanism of the Special Salt Effect[2-4]

BY S. WINSTEIN, PAUL E. KLINEDINST, JR., AND G. C. ROBINSON

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For the mechanism of the special effect of non-common ion salts in acetolysis of certain arenesulfonates, there were previous strong indications against some type of "physical" explanation. The occurrence of induced common ion rate depression by added common ion salts supports a mechanism for the special salt effect involving diversion of a carbonium ion pair to a new ion pair species, thus suppressing ion pair return. The kinetic form of the special salt effect and induced depression is appropriate for this mechanism. Also, it shows that the ion pair exchanges responsible for the special salt effect and induced depression phenomena involve ion pairs of the added salts. The parameters derived from the kinetics of the special salt effect and induced depression in acetolysis of 1-anisyl-2-propyl and 3-anisyl-2-butyl arenesulfonates provide considerable insight into the magnitude of various rate ratios and equilibrium constants connected with the solvolysis scheme. Ingold's interpretation of the nucleophilic substitution and exchange reactions of trityl chloride in benzene is discussed and criticized.

As illustrated in solvolysis scheme I, it is helpful to distinguish between three varieties of carbonium ion intermediate in acetolysis of various systems,[5,6] the intimate and solvent-separated ion pairs II and III, respectively, and the dissociated carbonium ion IV. Scheme I is designed for systems such as those with which we are concerned in the present

manuscript, where solvolysis product ROS is visualized[1a,b,6,7] to arise from solvent-separated ion pair III and also the dissociated carbonium ion IV when the latter is formed. Return[5,6] of carbonium ion intermediates toward covalent RX may occur from the dissociated carbonium ion stage (external ion return) or from ion pairs (ion pair return).[6] Ion pair return may be further dissected[6,7] into return from the intimate ion pair (internal return) and return from the solvent-separated ion pair (external ion pair return).

Certain systems in acetolysis respond to the addition of salts like lithium perchlorate with a combination of steep special[1a–c,6,7,8] salt effects at low concentrations of added salt and the more shallow linear normal[1d,6,9] salt effects at higher concentrations of salt. It is clear that the special salt effect is concerned with prevention of ion pair return.[1a–c,6–9] However, in acetolysis of several systems examined in detail, namely, the 3-anisyl-2-butyl,[7] 2-anisy-1-propyl,[1a] 2-anisyl-1-ethyl[1b] and 4-methoxy-1-pentyl[1c] arenesulfonates, the elimination of ion pair return

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(2) Presented in part at: (a) VIth Reaction Mechanism Conference, Swarthmore, Pa., Sept. 12, 1956; (b) VIIIth Mendeleev Congress of Pure and Applied Chemistry, Moscow, U.S.S.R., March, 1959.

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(4) Research sponsored by the Office of Ordnance Research, U. S. Army.

(5) (a) W. G. Young, S. Winstein and H. L. Goering. THIS JOURNAL, 73, 1958 (1951); (b) S. Winstein and D. Trifan, ibid., 74, 1154 (1952); (c) S. Winstein and K. C. Schreiber, ibid., 74, 2165, 2171 (1952).

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(7) S. Winstein and G. C. Robinson, ibid., 80, 169 (1958).

(8) (a) A. H. Fainberg and S. Winstein, ibid., 78, 2767 (1956); (b) S. Winstein and E. Clippinger, ibid., 78, 2784 (1956).

(9) (a) A. H. Fainberg and S. Winstein, ibid., 78, 2763 (1956); (b) A. H. Fainberg and S. Winstein, ibid., 78, 2780 (1956).