π-Complexed β-Arylalkyl Derivatives. IV. The Preparation and Solvolysis of 2-[π-(Phenyl)chromium tricarbonyl]ethyl and 2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonates and Their Noncomplexed Analogs[1a]

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The π-(arene)chromium tricarbonyl complexed methanesulfonates 2-phenylethyl (**2**-OMs), 2-phenylethyl-*1,1*-d_2 (**4**-OMs), and 2-phenyl-1-propyl (*dl*-**6**-OMs) have been prepared and their acetolysis and formolysis rates and/or products compared with those of the noncomplexed derivatives, 1-OMs, **3**-OMs, and *dl*-**5**-OMs, respectively. At ~90° in buffered acetic acid, **2**- is ten times as reactive as 1-OMs, *dl*-**6**- about six times as reactive as *dl*-**5**-OMs; in buffered formic acid **2**- is 8.5 times more reactive than 1-OMs, *dl*-**6**- 2.4 times more reactive than *dl*-**5**-OMs. The formolysis of *dl*-**6**-OMs yields 17% [π-(phenyl)chromium tricarbonyl]-migrated product; the formolysis of **4**- and the acetolysis of **4**- and *dl*-**6**-OMs yield unrearranged products exclusively. By comparing Fk_Δ's of the complexes with those of the corresponding noncomplexed *p*-nitro derivatives, estimates of anchimeric assistance to product formation by β-[π-(phenyl)chromium tricarbonyl] have been deduced: **2**-OMs, 10^4 (HOAc), $10^{3.6}$ (HCOOH); *dl*-**6**-OMs, $10^{3.2}$ (HOAc), $10^{3.1}$ (HCOOH). Steric buttressing effects are considered to be relatively unimportant and electron donation by the π-complexed phenyl moiety is suggested as the probable cause of these effects.

In previous papers of this series[2] we reported the acetolytic rates and products of a series of chromium tricarbonyl complexed 3-phenyl-2-butyl, 2-phenyl-3-pentyl, and neophyl-type methanesulfonates. After making a correction for the apparent inductive effect of the tricarbonylchromium group, we concluded that the acetolytic reactivity of the complexes was enhanced by factors of from 6.8 to 1600 times at 75°. We were able to infer that a substantial portion of the enhancement is due to an electronic effect of the metal moiety, but were unable to evaluate the magnitude of the steric effect on these reactions.[2b]

One of the techniques that has been effectively used to detect and establish the importance of neighboring group participation in solvolytic reactions is that of varying the nucleophilicity and ionizing power of the solvent.[3-12] Thus it is generally accepted that both the importance of kinetic neighboring group participation and the extent of rearrangement increase as the solvent becomes less nucleophilic and/or more ionizing, *i.e.*, in the order ethanol < acetic acid < formic acid < trifluoroacetic acid < sulfuric acid < fluorosulfonic acid. The good linear free energy correlations that have been obtained for both the assisted and the unassisted processes[2b] strongly imply that the driving force for participation is predominantly electronic rather than steric in nature.

In an effort to confirm its importance and assess the nature of tricarbonylchromium participation during the solvolysis of β-[π-(aryl)chromium tricarbonyl]alkyl derivatives, we have examined the acetolysis and formolysis rates and/or products of 2-phenylethyl (**1**-OMs), 2-[π-(phenyl)chromium tricarbonyl]ethyl (**2**-OMs), 2-phenyl-*1,1*-d_2-ethyl (**3**-OMs), 2-[π-(phenyl)-chromium tricarbonyl]-*1,1*-d_2-ethyl (**4**-OMs), 2-phenyl-1-propyl (*dl*-**5**-OMs), 2-[π-(phenyl)chromium tricarbonyl]-1-propyl (*dl*-**6**-OMs), 2-(*p*-nitrophenyl)ethyl (**7**-OMs), and 2-(*p*-nitrophenyl)-1-propyl (*dl*-**8**-OMs) methanesulfonates.

Methods and Results

The known noncomplexed alcohols, **1**-, **3**-, *dl*-**5**-, **7**-, and *dl*-**8**-OH, obtained as described in the Experimental Section, were converted to methanesulfonates in the usual manner.[2a] The chromium tricarbonyl complexes, **2**-, **4**-, and *dl*-**6**-OMs were prepared as described previously[2a] (*cf.* Chart I).

Acetolysis products, determined by combination of the direct analysis, decomplexation, and reduction techniques described previously,[2a] are summarized in Chart II.

Formolysis products, determined in a similar manner (*cf.* Experimental Section), are summarized in Chart III. As noted previously,[2] chromium tricarbonyl complexation prior to solvolysis inhibits phenyl migration; only during the formolysis of *dl*-**6**-OMs is a significant amount of rearranged product formed.

Titrimetric acetolysis and formolysis constants for the complexed and noncomplexed methanesulfonates were determined as detailed previously[2] and in the Experimental Section at concentrations similar to those

(1) (a) Portions of this work were presented at the 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969, Abstract No. 277; (b) NSF Summer Faculty Research Participant, 1969.

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(3) (a) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952); (b) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953); (c) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3506 (1965); (d) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1968); (e) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968); (f) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); (g) I. Lazdins, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969); (h) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, 5637 (1969).

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(9) (a) C. J. Lancelot and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291 (1969); (b) *ibid.*, **91**, 4296 (1969); (c) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); (d) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969); (e) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969).

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(11) R. J. Jablonski and E. I. Snyder, *J. Amer. Chem. Soc.*, **91**, 4445 (1969).

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Chart I

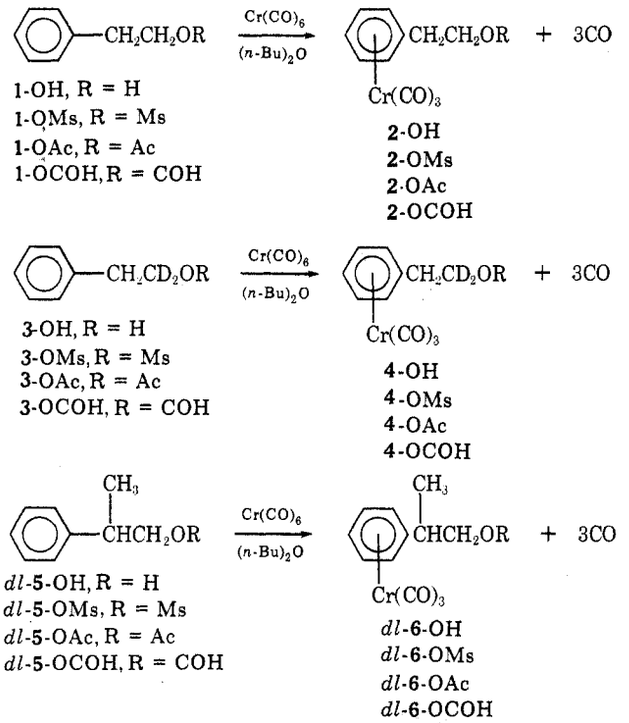
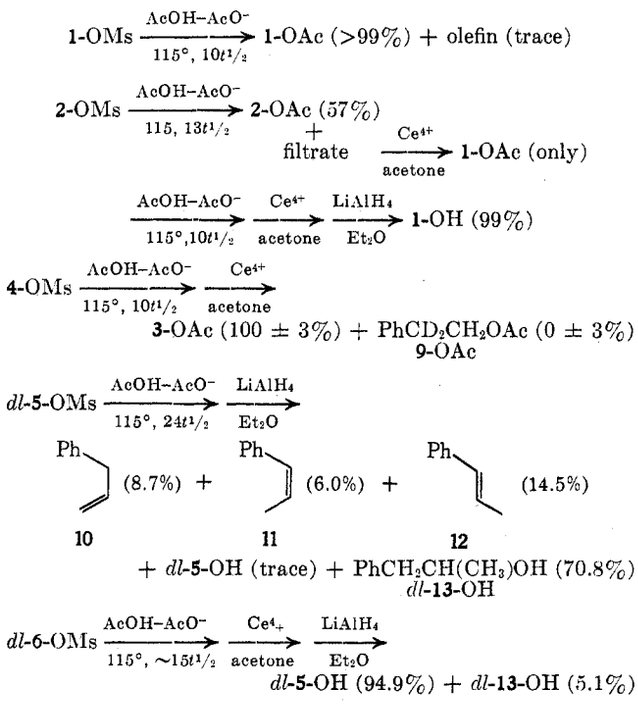


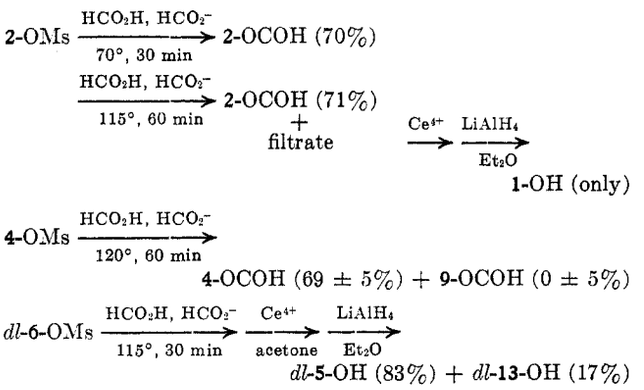
Chart II



used in the product studies. These data are summarized and compared with those of some related noncomplexed derivatives[3b,9e,13,14] in Table I. With the exception of the acetolysis of *dl*-5-OMs, *cf.* runs 41 and 42, each of the solvolyses exhibited clean first-order kinetics through at least 75% reaction.

The effects of added salts on the acetolysis rates of 1-, 2-, 7-, and *dl*-8-OMs are recorded in Table II.[15]

Chart III



Discussion

The fact that in both the β-arylethyl and the 2-arylpropyl series the ratios of the relative titrimetric rate constants for solvolysis of the complexed and noncomplexed methanesulfonates at 86.6° do not change markedly as the solvent is changed from acetic to formic acid, *viz.*, k_t(2-OMs)/k_t(1-OMs), 17.4/1.68 = 10.4 (HOAc), 1117/131.7 = 8.5 (HCOOH); k_t(6-OMs)/k_t(5-OMs), 47.6/7.81 ≈ 6.1 (HOAc), 2990/1270 ≈ 2.4 (HCOOH), implies at first glance that the enhanced reactivity of the former might more properly be attributed to steric than to electronic factors. However, this view is certainly oversimplified and probably incorrect, for it fails to consider the substantial electron-withdrawing inductive effect of the π-tricarbonylchromium and the extent to which the solvolyses are accompanied by nucleophilic solvent participation.

The solvolyses of noncomplexed β-arylalkyl derivatives in the absence of added base have been successfully interpreted in terms of the discrete, competing solvent- and aryl-assisted pathways represented in Chart IV,[3c-e,9e,12a,13,16] where F is the fraction of bridged ion pairs which is converted to product, Chart IV, so that $k_t = Fk_\Delta + k_s$. Thus, when comparing the relative abilities of differing aryl groups to enhance the rate of product formation through neighboring-

Chart IV

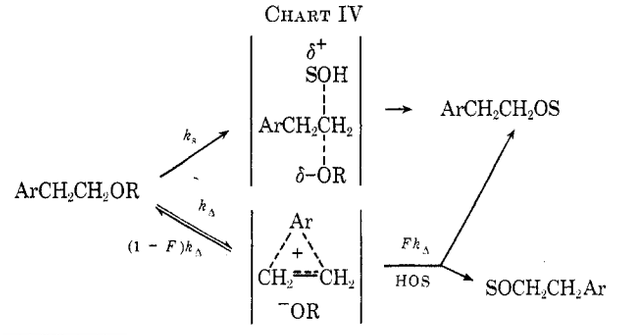


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TABLE I

APPARENT FIRST-ORDER SOLVOLYSIS CONSTANTS AND ACTIVATION PARAMETERS OF 2-ARYL-1-ETHYL AND -1-PROPYL DERIVATIVES[a]

Run	Compd	Solvent	Temp, °C[b]	10^5k_t, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
1, 2	1-OMs	AcOH/AcO$^-$ [c]	85.0	1.405 ± 0.045	24.9[d]	−16.2[d]
3, 4			97.3	4.605 ± 0.015		
5, 6			115.1	23.0 ± 0.00		
7			115.2	11.9[e]		
8			115.3	19.0[f]		
9				27.4[g]		
			86.7	1.68[h]		
			90.0	2.31[h]		
	1-OTs[aa]			1.28	24.9	−17.3
10, 11	1-OMs	HCO_2H/HCO_2^- [i]	86.7	131.65 ± 0.05		
	1-OTs[j]		86.6	111		
12, 13	2-OMs	AcOH/AcO$^-$ [c]	85.0	14.5 ± 0.4	24.5[k]	−12.5[k]
14, 15			97.4	49.7 ± 0.5		
16			113.0	42.1[e]		
17				42.6[e,l]		
18, 19			115.0	227.5 ± 5.5		
20			115.2	64.9[e]		
21			115.3	227[m]		
			86.7	17.4[h]		
			90.0	24.0[h]		
			115.3	236[h]		
22–24		HCO_2H/HCO_2^- [i]	86.7	1117 ± 19		
25	4-OMs		86.7	902[n]		
26			86.8	889		
27, 28	7-OMs	AcOH/AcO$^-$ [c]	86.95	2.00 ± 0.00	22.4[o]	−22.9[o]
29, 30			113.1	18.0 ± 0.15		
31			113.15	26.3[p]		
32				32.1[q]		
33			113.2	12.9[r]		
34			113.4	6.2[e]		
			86.7	1.97[h]		
			90.0	2.64[h]		
	7-OTs[bb]			0.715	23.7	−22
35, 36	7-OMs	HCO_2H/HCO_2^- [i]	69.25	1.275 ± 0.025	21.3[s]	−23.6[s]
37, 38			86.2	6.015 ± 0.045		
39, 40			99.4	17.4 ± 0.1		
			86.7	6.16[h]		
41, 42	*dl*-5-OMs	AcOH/AcO$^-$ [c]	86.65	~7.81 ± 0.17[t]		
	dl-5-OBs[cc]		86.7[h]	35.0	25.5	−8.5
			90.0[h]	48.8		
43, 44	*dl*-5-OMs	HCO_2H/HCO_2^- [i]	86.4	1270 ± 20		
45, 46	*dl*-6-OMs	AcOH/AcO$^-$ [c]	69.3	7.165 ± 0.165	26.3[u]	−5.5[u]
47, 48			86.8	48.85 ± 0.85		
49, 50			112.45	609 ± 9		
			86.5	47.6[h]		
			90.0	68.5[h]		
51, 52		HCO_2H/HCO_2^- [i]	86.45	2990 ± 80		
53, 54	*dl*-8-OMs	AcOH/AcO$^-$ [c]	99.8	0.6115 ± 0.0115	25.6[v]	−18.8[v]
55–57			115.1	2.26 ± 0.18		
58				3.74[w]		
59				3.32[x]		
60				1.99[y]		
61				1.15[e]		
62, 63			130.0	8.875 ± 0.065		
			86.7	0.167[h]		
			90.0	0.233[h]		
64, 65		HCO_2H/HCO_2^- [i]	69.25	0.226 ± 0.000	26.6[z]	−11.6[z]
66, 67			86.2	1.51 ± 0.005		
68, 69			99.4	5.81 ± 0.06		
			86.7	1.58[h]		

[a] Contains 0.0185–0.0250 *M* ROMs unless otherwise specified. [b] Controlled to ±0.03°. [c] Contains 0.0461–0.0508 *M* sodium acetate unless otherwise specified. [d] Computed from runs 1–6. [e] Contains no sodium acetate. [f] Contains 0.0286 *M* sodium acetate. [g] Contains 0.0327 *M* lithium perchlorate. [h] Calculated from data at other temperatures. [i] Contains 0.0250–0.0350 *M* sodium formate unless otherwise specified. [j] Extrapolated from the data in ref 3b and 13c. [k] Calculated from runs 12–15, 18, and 19. [l] Contains 0.0203 *M* sodium methanesulfonate. [m] Contains 0.0286 *M* sodium acetate. [n] Contains 0.0141 *M* ROMs. [o] Calculated from runs 27–30. [p] Contains 0.0772 *M* sodium acetate. [q] Contains 0.0989 *M* sodium acetate. [r] Contains 0.0302 *M* sodium acetate. [s] Calculated from runs 35–40. [t] Since this reaction is accompanied by extensive internal return to the more reactive *dl*-**13**-OMs, this constant was approximated from the first 20% reaction (*cf.* ref 14). [u] Calculated from runs 45–50. [v] Calculated from runs 53–57, 62, and 63. [w] Contains 0.0950 *M* sodium acetate. [x] Contains 0.0752 *M* sodium acetate. [y] Contains 0.0326 *M* sodium acetate. [z] Calculated from runs 64–69. [aa] Reference 3b. [bb] Reference 9e. [cc] Reference 14.

Table II
Dependence of Apparent First-Order Acetolysis Constants of 2-Aryl-1-ethyl and 2-Aryl-1-propyl Type Sulfonates upon Added Salts

Compd	Temp, °C	$10^6 k_t°$,[a] sec^{-1}	Value of "b" for added NaOAc[b]
1-OMs	115.2	12.5	18[c,d]
1-OTs[i]	115	13.0	19
2-OMs	115.2	217	1.9[e,f]
7-OMs	113.2	4.35	64[g]
8-OMs	115.1	0.93	30[h]

[a] Extrapolated value at zero acetate concentration. [b] Calculated from the relation $k_t = k_t°(1 + b_1[\text{NaOAc}] + b_2[\text{salt 2}])$.[15] [c] Calculated from runs 5, 6, and 8; $(k_t°)_{\text{extrapolated}} = 1.05\ (k_t°)_{\text{measured}}$. [d] $b(\text{LiClO}_4) \approx 11$ (*cf.* runs 5, 6, and 9). [e] Calculated from run 21 and an interpolated value at this temperature for 0.0401 *M* sodium acetate; $(k_t°)_{\text{extrapolated}} = 3.35\ (k_t°)_{\text{measured}}$. [f] $b(\text{NaOMs}) \approx 0$ (*cf.* runs 16 and 17). [g] Calculated from runs 29–33; $(k_t°)_{\text{extrapolated}} = 0.70\ (k_t°)_{\text{measured}}$. [h] Calculated from runs 55–60; $(k_t°)_{\text{extrapolated}} = 0.81\ (k_t°)_{\text{measured}}$. [i] Reference 3b.

group participation during solvolysis, it is apparent that Fk_Δ's rather than k_t's should be employed.[12,17]

In previous papers in this series we have taken the titrimetric rate constant of the *p*-nitro derivative as a model for that of the π-complexed derivative in the absence of participation.[2] This treatment appeared to yield reasonable estimates of π-complexed aryl participation, since in the systems considered, *viz.*, 3-aryl-2-butyl[2a,18] and neophyl,[2b,15] direct displacement by solvent is relatively unimportant. However, in the solvolyses of β-arylethyl and 2-arylpropyl derivatives direct solvent participation is frequently the dominant reaction.[3f,5a,12a,13a,14] Hence, estimates, not of titrimetric rate constants, k_t, but of the rate constants Fk_Δ, for product formation *via* the bridged ion pair are desired.[12a] These may be estimated from experimental data reported here and elsewhere as follows.

Acetolysis of β-[π-(Phenyl)chromium tricarbonyl]-ethyl Methanesulfonate (2-OMs).—Jones and Coke have demonstrated the existence of a good linear correlation between log k_t for the acetolysis of para-substituted neophyl tosylates at 75° and log k_Δ for the acetolysis of like-substituted β-arylethyl tosylates at the same temperature,[12b] *viz.*, $\log k_\Delta(\beta\text{-arylethyl}) = 1.02 \log k_t(\text{neophyl}) - 1.85$.[19a] Since, as Jones and Coke[12b] have determined from rate and product data and Schleyer, *et al.*, have derived from rate data alone, "*F* is nearly constant for all participating substrates,"[9e] a plot of log k_t(neophyl) *vs.* log k_Δ(β-arylethyl) should also be linear[19b] and have a slope of approximately unity.[19c] The plot shown in Figure 1, which is based on the acetolysis rates at 90° (Table III), confirms this expectation.

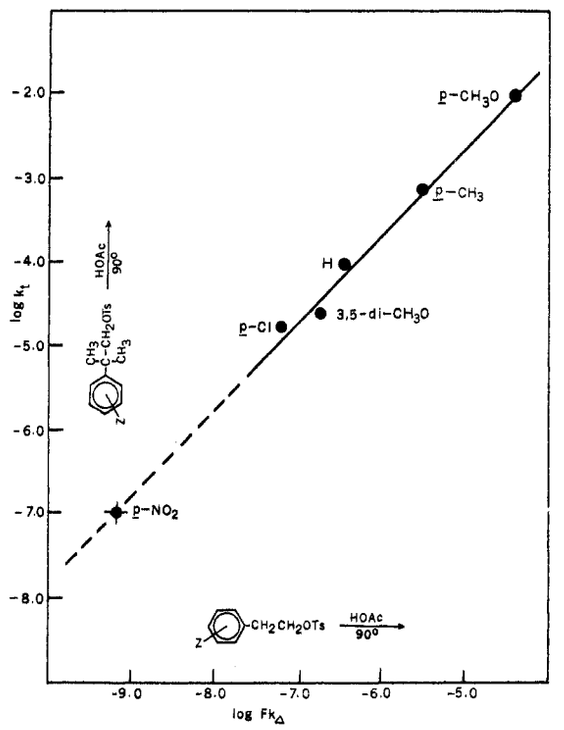


Figure 1.—Acetolysis of substituted β-arylethyl and neophyl tosylates at 90°, 0.00 *M* acetate ion.

Table III
Acetolysis Rates of Substituted β-Arylethyl and Neophyl Tosylates at 90°[a]

Substituent	β-Arylethyl Fk_Δ, sec^{-1}	Neophyl k_t, sec^{-1}
p-CH_3O	4.65×10^{-5} [b]	8.93×10^{-3} [c]
p-CH_3	3.19×10^{-6} [b]	7.25×10^{-4} [c]
H	3.75×10^{-7} [b]	9.57×10^{-5} [c]
3,5-di-CH_3O	2.15×10^{-7} [d]	2.36×10^{-5} [e]
p-Cl	6.99×10^{-8} [b]	1.87×10^{-5} [c]
p-NO_2		9.93×10^{-8} [f]

[a] At 0.00 *M* sodium acetate. [b] Reference 12b. [c] Extrapolated value from data in ref 12b. [d] Reference 16b. [e] Estimated as k_t(ROBs)/3.49, where k_t(ROBs) is calculated from the Yukawa–Tsuno relation, $\log k_t = -3.711[\sigma + 0.4828(\sigma^+ - \sigma)] - 3.478$, for the acetolysis of neophyl-type brosylates at 90° (*p*-CH_3O, *p*-CH_3, *m*-CH_3, H, *m*-CH_3O, *p*-Cl, *p*-Br, *p*-CO_2CH_3, *p*-CN, *p*-NO_2) assuming that σ(3,5-di-CH_3O) = 2σ(*m*-CH_3O) = 0.230 and σ^+(3,5-di-CH_3O) = $2\sigma^+$(*m*-CH_3O) = 0.094. [f] Estimated from k_t of the brosylate corrected for the extent of *p*-nitrophenyl migration assuming that the fraction of aryl-migrated products (0.75) is similar for the brosylate at 137° and the brosylate at 90° [20] and that k_t(ROTs) = k_t(ROBs)/3.49.

Extrapolation of the resulting double least squares regression line,[19d] $\log (Fk_\Delta°) = 0.998 \log (k_t°) - 2.327$ (which is linear over approximately three powers of ten), through the estimated k_t[19e] for *p*-nitroneophyl (another two powers of ten, Table III)[19f] yields an Fk_Δ of 4.85×10^{-10} sec^{-1} for the acetolysis of β-(*p*-nitrophenyl)ethyl *p*-toluenesulfonate (7-OTs) at 90°

(17) We emphasize that the *overall* effect of neighboring-group participation *on the rate of product formation* is given by Fk_Δ and is a composite of the effect of the neighboring group on *F*, the fraction of bridged ion pair going on to product, and on k_Δ, the rate of ionization; *cf.* ref 9d, footnote 14.

(18) (a) D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 3767 (1964), and references cited therein; (b) S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964).

(19) (a) This empirical equation is a special case of the more general relation log (Fk_Δ)(neophyl) = log (Fk_Δ)(β-arylethyl) + *C*, and is valid apparently because nucleophilic solvent participation is relatively unimportant for all but the least reactive neophyl derivatives,[3f,9c,20] so that for this series $k_t = Fk_\Delta$, because the anchimeric assistance to ionization provided by the β-aryl group is proportional in the two series of compounds, *i.e.*, k_Δ(neophyl) ∝ k_Δ(β-arylethyl) (the proportionality constant is incorporated into the intercept, *C*) and because the fraction, *F*, of ion pairs going on to product in the neophyl case is constant—though not necessarily unity—over the range of substituents tested. (b) *Cf.* ref 9e, footnote 17. (c) The only significance that can properly be attributed to the unitary slope of an empirical log–log correlation such as this is that the proportionality relationships[19a] are maintained throughout the range of substituents tested. (d) All rate constants are corrected to zero acetate ion concentration. (e) Corrected for the extent of direct displacement so that the value of k_t used here and quoted in Table III is actually Fk_Δ; *cf.* ref 3f, footnote 13. (f) Note that the validity of this extrapolation is dependent not upon *F* for β-(*p*-nitrophenyl)ethyl remaining unchanged, but rather upon the ratio *F*[β-(*p*-nitrophenyl)ethyl]/*F*(*p*-nitroneophyl) remaining approximately constant.

(20) H. Tanida, T. Tsuji, H. Ishitobi, and T. Irie, *J. Org. Chem.*, **34**, 1086 (1969).

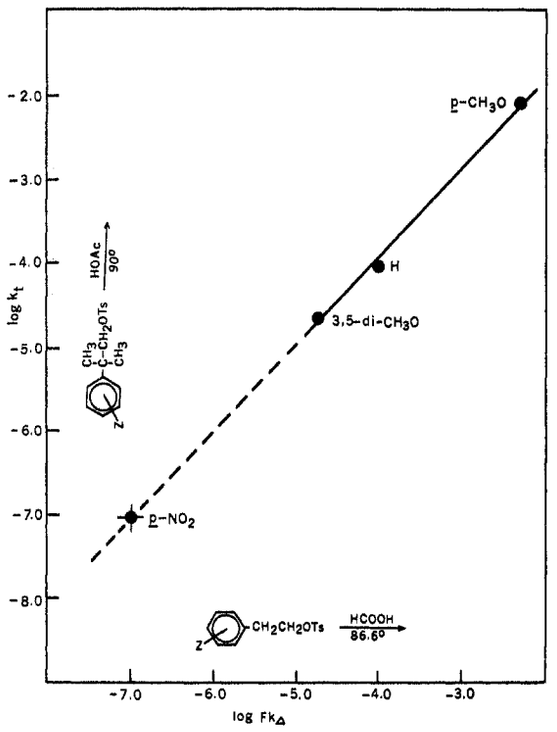


Figure 2.—Formolysis of substituted β-arylethyl tosylates at 86.6° *vs.* acetolysis of like-substituted neophyl tosylates at 90°, 0.00 *M* base.

in the absence of added sodium acetate. Since $k_s^\circ = k_t^\circ - Fk_\Delta^\circ = 7.15 \times 10^{-7} - 4.85 \times 10^{-10} = 7.15 \times 10^{-7}$ sec^{-1}, it is apparent that *p*-nitrophenyl participation is relatively unimportant under these conditions.[9e] Correction of our data (Table II) for the acetolysis of the corresponding mesylate (7-OMs) at 90° in the presence of added sodium acetate yields estimates of 8.9×10^{-7}, 8.9×10^{-7}, and 5.6×10^{-10} sec^{-1}, respectively, for k_t°, k_s°, and Fk_Δ° at zero acetate ion concentration.[21] A similar correction applied to the titrimetric acetolysis rate of β-[π-(phenyl)chromium tricarbonyl]ethyl methanesulfonate (2-OMs) (Table II) yields an estimated k_t° at 90°, zero acetate ion concentration, of 6.5×10^{-6} sec^{-1}.

The inductive effects of *p*-nitrophenyl and π-phenylchromium tricarbonyl are similar,[22] while the steric bulk of the latter is not less than that of the former; thus it follows that the solvent-assisted rate constant in the absence of base, k_s°, of 7-OMs constitutes an upper limit for k_s° (2-OMs) under comparable conditions, *i.e.*, k_s°(7-OMs) $\approx k_t^\circ$(7-OMs) $\approx 8.9 \times 10^{-7}$ sec^{-1} $\geqslant k_s^\circ$(2-OMs). Therefore Fk_Δ° for the acetolysis of 2-OMs at 90° in the absence of added acetate must be equal to or greater than k_t°(2-OMs) $- k_s^\circ$(7-OMs) $\geqslant 6.5 \times 10^{-6} - 8.9 \times 10^{-7} \geqslant 5.6 \times 10^{-6}$ sec^{-1}. Comparison of Fk_Δ°(2-OMs) and Fk_Δ°(7-OMs) provides an estimate of the relative ability of π-(phenyl)chromium tricarbonyl and *p*-nitrophenyl to enhance the rate of product formation during acetolysis at 90°; *i.e., the complexed aryl is 5.6 × 10^{-6}/5.6 × 10^{-10} or ~10,000 times more effective.*

The rate constant for product formation *via* the internally assisted acetolysis (Fk_Δ°) of β-phenylethyl methanesulfonate (1-OMs) at 90° and zero acetate ion concentration, estimated in a similar manner from that of the tosylate (1-OTs),[3b] is 4.4×10^{-7} sec^{-1}. Thus, the π-complexed phenyl, in spite of its large rate-retarding inductive effect, is $5.6 \times 10^{-6}/4.4 \times 10^{-7}$ or 13 times more effective than phenyl itself in promoting product formation under these conditions.

Formolysis of β-[π-(Phenyl)chromium tricarbonyl]-ethyl Methanesulfonate (2-OMs).—We are prevented by the lack of sufficient data in this solvent from utilizing an analogous method to estimate the rate enhancement which accompanies the formolysis of 2-OMs. Diaz and Winstein[3f] have, however, demonstrated the existence of a good linear correlation between log k_Δ° of *formolysis* for para-substituted 1-phenyl-2-propyl tosylates at 75° and log k_t of *acetolysis* for like-substituted neophyl tosylates under similar conditions. Thus it is reasonable to expect that a similar correlation would exist between log Fk_Δ° of formolysis for para-substituted β-phenylethyl tosylates at 86.6° and log k_t of acetolysis for like-substituted neophyl derivatives at 90°.[23] Such a plot, based on the data of Table IV, is shown in Figure 2. Extrapolation of the correlation line fitted to the data by a double least squares regression analysis, log $(Fk_\Delta^\circ) = 0.944 \log k_t - 0.323$, through k_t for *p*-nitro (Table IV) yields an estimated Fk_Δ° of 1.2×10^{-7} sec^{-1} for the formolysis of 7-OTs at 86.6° in the absence of added base. The predicted Fk_Δ° for the corresponding mesylate (7-OMs) under these conditions would be $1.16 \times 1.2 \times 10^{-7}$ or 1.4×10^{-7} sec^{-1}. The titrimetric formolysis constant, k_t, of 7-OMs at 86.6° in the presence of 0.035 *M* sodium formate is 6.07×10^{-6} sec^{-1} (Table I). Although *b* values have not been determined in this solvent system, that of the anchimerically assisted process, Fk_Δ, can be expected to be relatively small so that $k_s \approx k_t - Fk_\Delta^\circ \approx 6.07 \times 10^{-6} - 1.4 \times 10^{-7} \approx 5.9 \times 10^{-6}$ sec^{-1} at 86.6° in the presence of 0.035 *M* formate ion. Thus under these conditions about 2% of the products are apparently formed *via* a *p*-nitrophenyl-bridged ion pair. The titrimetric formolysis constant, k_t, of 2-OMs under similar conditions is 1117×10^{-6} sec^{-1}, so that Fk_Δ for the complex equals $1117 \times 10^{-6} - k_s$(2-OMs) $\geqslant 1117 \times 10^{-6} - k_s$(7-OMs) $\approx 1117 \times 10^{-6} - 5.9 \times$

TABLE IV
SOLVOLYSIS RATES OF β-ARYLALKYL-TYPE TOSYLATES

Substituent	β-Arylethyl formolysis, 86.6°, Fk_Δ, sec^{-1}	Neophyl acetolysis, 90°, k_t, sec^{-1}
p-CH$_3$O	4.96×10^{-3} [a]	8.93×10^{-3} [b]
H	9.93×10^{-5} [c]	9.57×10^{-5} [b]
3,5-di-CH$_3$O	1.86×10^{-5} [d]	2.36×10^{-5} [e]
p-NO$_2$		9.93×10^{-8} [f]

[a] Extrapolated from data at other temperatures, 0.000–0.055 *M* sodium formate; *cf.* ref 3b and 3c. [b] Extrapolated from the data in ref 12b. [c] Calculated from k_t at other temperatures, 0.000–0.0291 *M* sodium formate, assuming $Fk_\Delta = k_t/0.91$, *cf.* ref 3b, 13a, and 16b, and $k_\Delta/(k_\Delta + k_s) = 0.90$, *cf.* ref 3c. [d] Estimated from data on the brosylate interpolated from other temperatures, *cf.* ref 13a and 16b, assuming k_t(OBs) = 2.50 k_t(OTs), *cf.* ref 13a, and that the fraction of products formed *via* the bridged ion in the case of the brosylate at 75°, *i.e.*, 52%, equals that from the tosylate at 86.6°, *cf.* ref 16b. [e] Table III, footnote *e*. [f] Table III, footnote *f*.

(21) In agreement with Schleyer, *et al.*,[9e] we note that the value of Fk_Δ for acetolysis of 7-OMs, though small, is not zero; *cf.* Table II, ref 9b.

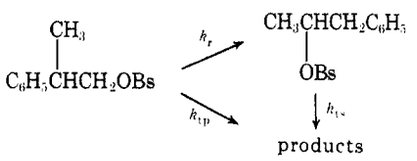
(22) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(23) Note that because the solvents and temperatures are different, the slope of such a correlation line is no longer unity; *cf.* ref 3f, Figure 2.

$10^{-6} \geq 1111 \times 10^{-6}$ sec^{-1}. Hence π-tricarbonylchromium enhances the rate of product formation during formolysis by a factor of $1111 \times 10^{-6}/1.4 \times 10^{-7} = 7900$ times compared to *p*-nitro. Similarly (*cf.* Table IV), the complexed mesylate is enhanced by a factor of $(1111 \times 10^{-6})/(1.16 \times 9.93 \times 10^{-5}) = 9.6$ times with respect to the β-phenylethyl derivative (1-OMs).

Acetolysis of 2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonate (*dl*-**6-OMs**).—Attempts to estimate the rate enhancement due to π complexation in this system are complicated by two factors: the occurrence of extensive internal return to the more reactive 1-phenyl-2-propyl isomer in the case of *dl*-**5**-OR[3b,f,14] and the lack of suitable kinetic data for substituted phenyl derivatives. The following approach seems best under the circumstances. Assuming that the acetolyses of both **7**- and *dl*-**8**-OTs at 90° occur predominantly *via* the solvent-assisted pathway, k_s,[9e,24] the ratio of their titrimetric rate constants, k_t, at this temperature (Table I) represents the steric effect of the β-methyl group upon the solvent-assisted reaction. Hence k_s(*dl*-**5**-OTs) $\approx [k_t(dl\text{-}\mathbf{8}\text{-OMs})/k_t(\mathbf{7}\text{-OMs})] \cdot k_s$(1-OTs)[25] $= [(2.33 \times 10^{-7})/(2.64 \times 10^{-6})](8.92 \times 10^{-7}) = 7.87 \times 10^{-8}$ sec^{-1}. Winstein, *et al.*, have carried out a detailed kinetic analysis of the acetolysis of *dl*-**5**-OBs within the kinetic framework shown in Chart V.[14]

CHART V



Since

$$\frac{-\mathrm{d}[\text{2-aryl-1-propyl}]}{\mathrm{d}t} = (k_r + k_{tp})[\text{2-aryl-1-propyl}]$$

while

$$\frac{-\mathrm{d}[\text{neophyl}]}{\mathrm{d}t} = k_t[\text{neophyl}] = (Fk_\Delta + k_s)[\text{neophyl}]$$

it seems appropriate to equate $(k_r + k_{tp})$ for 2-aryl-1-propyl derivatives with k_t for systems whose solvolysis is not accompanied by extensive internal return to a more reactive isomer, *i.e.*, $k_r + k_{tp} = k_t = Fk_\Delta + k_s$. Thus, at 90° Fk_Δ(*dl*-**5**-OTs) $= k_t$(*dl*-**5**-OTs) $= (k_r + k_{tp})$(*dl*-**5**-OTs) $- k_s$(*dl*-**5**-OTs) $= 1.67 \times 10^{-5}$ [26] $- 7.87 \times 10^{-8} \approx 1.67 \times 10^{-5}$ sec^{-1}.

For the aryl-assisted acetolysis of *dl*-**8**-OTs, Fk_Δ at 90° can be approximated as follows. Both β-arylethyl and 2-aryl-2-methyl-1-propyl (neophyl) tosylates give correlation lines of unit slope (*cf.* Figure 1) when values of log Fk_Δ for acetolysis at 90° are plotted against values of log k_t for like-substituted 2-aryl-2-methyl-1-propyl tosylates under similar conditions.[19c] It follows that the structurally intermediate 2-aryl-1-propyl tosylates should also be related to like-substituted 2-aryl-2-methyl-1-propyl tosylates in a similar manner, *i.e.*, that log Fk_Δ(2-aryl-1-propyl tosylate, HOAc, 90°) = 1.0 log k_t(2-aryl-2-methyl-1-propyl tosylate, HOAc, 90°) + C. This being true, the constant C can be computed from the value of Fk_Δ(*dl*-**5**-OTs) estimated previously and the measured k_t of neophyl tosylate (Table III), *viz.*, for acetolysis at 90° log $(1.67 \times 10^{-5}) = 1.0$ log $(9.57 \times 10^{-5}) + C$, or $C = -0.7582$, so that the equation for the expected correlation becomes log Fk_Δ(2-aryl-1-propyl tosylate, HOAc, 90°) = log k_t(2-aryl-2-methyl-1-propyl tosylate, HOAc, 90°) − 0.7582.

Using this equation and the estimated acetolysis constant, k_t, for *p*-nitroneophyl tosylate at 90° (Table III), a value for Fk_Δ(*dl*-**8**-OTs) under these conditions can be predicted, *viz.*, log Fk_Δ(*dl*-**8**-OTs) = log $(9.93 \times 10^{-8}) - 0.7582$ or Fk_Δ (*dl*-**8**-OTs, HOAc, 90°) $= 1.7 \times 10^{-8}$ sec^{-1}.

Schleyer[9e] has demonstrated that the solvent-assisted rate constant, k_s, for the acetolysis of a β-arylethyl tosylate at 90° can be computed from the Hammett relation log $k_s = -0.115\sigma +$ log k_s^H. It follows from this and our previous arguments that under similar conditions, *e.g.*, for acetolysis at 90°, k_s(*dl*-**5**-OTs) > k_s(*dl*-**8**-OTs) $\geq k_s$(*dl*-**6**-OTs), so that Fk_Δ(*dl*-**6**-OTs) $\geq k_t$(*dl*-**6**-OTs) $- k_s$(*dl*-**5**-OTs) or Fk_Δ(*dl*-**6**-OTs) $\geq (6.85 \times 10^{-5}/1.26)$[27] $- 7.87 \times 10^{-8} \geq 5.4 \times 10^{-5}$ sec^{-1}. Thus, π-phenylchromium tricarbonyl is $5.4 \times 10^{-5}/1.7 \times 10^{-8}$ or 3200 times more effective than *p*-nitrophenyl in promoting product formation during the acetolysis of 2-aryl-1-propyl derivatives at 90°. It is $5.4 \times 10^{-5}/1.67 \times 10^{-5}$ or 3.2 times more effective than phenyl itself.

Formolysis of 2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonate (*dl*-**6-OMs**).—Since there are essentially no kinetic data available for the formolysis of either 2-aryl-2-methyl-1-propyl or 2-aryl-1-propyl derivatives other than those reported here in the latter case, and since the assumption that the *p*-nitro derivatives solvolyze preponderantly *via* the solvent-assisted path may not be valid in formic acid, it seems best to estimate the effect of π complexation by direct comparison of the titrimetric rate constants at 86.6° (Table I). Thus, Fk_Δ(*dl*-**6**-OMs)/Fk_Δ(*dl*-**8**-OMs) $\approx k_t$(*dl*-**6**-OMs)/k_t(*dl*-**8**-OMs) $= 3000 \times 10^{-6}/1.6 \times 10^{-6}$ or 1900 times; Fk_Δ(*dl*-**6**-OMs)/Fk_Δ(*dl*-**5**-OMs) $\approx k_t$(*dl*-**6**-OMs)/k_t(*dl*-**5**-OMs) $= 3000 \times 10^{-6}/1270 \times 10^{-6}$ or 2.4 times.

The rate enhancements of solvolytic product formation induced by the prior chromium tricarbonyl complexation of primary β-arylethyl derivatives, estimated as the ratios of Fk_Δ(π complex)/Fk_Δ(*p*-nitro), are summarized in Table V.

In considering the possible implications of these data several questions come to mind. First and foremost: could these enhancements be due predominantly to steric effects? We think not. Chromium tricarbonyl complexation increases the absolute acetolytic reactivity at 85–90° by 10 times in the β-phenylethyl case, 6.1 times in the 2-phenyl-1-propyl derivative, and 1.6 times in the neophyl methanesulfonate. Thus the absolute rate enhancement is greatest in the least sterically congested β-phenylalkyl derivative and least in the most congested system. This is in spite of the fact that π complexation must certainly inhibit the

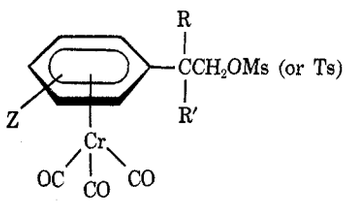
(24) *Cf.* acetate "*b*" values for the corresponding mesylates, Table II.

(25) Calculated from the data in ref 12b.

(26) Calculated by extrapolating the data in ref 14 (*cf.* Table I) and assuming that the measured acetolysis rate ratio, $(k_r + k_{tp})$(*dl*-**5**-OBs)/$(k_r + k_{tp})$(*dl*-**5**-OTs) = 2.92 at 75°,[3f] is maintained at 90°.

(27) Assuming that k_t(*dl*-**6**-OMs) = 1.26 k_t(*dl*-**6**-OTs); *cf.* Table I.

TABLE V
ESTIMATED SOLVOLYTIC RATE ENHANCEMENT DUE TO CHROMIUM TRICARBONYL COMPLEXATION



Z	R	R'	Solvent	Temp, °C	Enhancement[a]
H	H	H	HOAc	90	10,000[b]
			HCOOH	86.6	7,900[b]
H	CH_3	H	HOAc	90	3,200[b]
			HCOOH	86.6	1,900[b]
H	CH_3	CH_3	HOAc	75	1,600[c]
m-CH_3					800[c]
p-CH_3					400[c]
p-CH_3O					80[c]

[a] After correction for the rate-retarding inductive effect of the tricarbonylchromium; *vide supra*. [b] This work. [c] Reference 2b.

solvent-assisted process, k_s, to a greater extent in the less crowded β-phenylethyl methanesulfonate. Since the change in reactivity upon complexation is exactly opposite from that which would have been anticipated had steric butressing effects been dominant, we conclude that the rate factors which we have estimated in Table V are consonant with the idea of a relatively unimportant steric effect due to π complexation[28] coupled with some sort of electron-donating effect by the β-[π-(aryl)chromium tricarbonyl] group. We cannot on the basis of our data distinguish between the alternate possibilities of σ–π type homoconjugation or the direct chromium bridging suggested previously[2] as the manner in which this electronic effect is transmitted. We see no paradox in the fact that the estimated anchimeric effects of the π-(phenyl)chromium tricarbonyl during solvolysis are manifest in the absence of rearrangement, for in this sense the two primary π-complexed derivatives reported here resemble the secondary 1-aryl-2-propyl arenesulfonates studied by Winstein[3f] and by Schleyer.[9a–d] In each case the rate-limiting step of the reaction appears to be the formation of a nonsymmetric bridged cation–anion pair which reacts with the solvent to yield unrearranged products predominantly or exclusively.

A second question which these data raise concerns the relative extent of apparent participation by π-(phenyl)chromium tricarbonyl in acetic and in formic acid: it is slightly greater in the former than in the latter (Table V). Why? Our estimates of the magnitude of neighboring-group participation have involved numerous assumptions, some of which may at best be unwarranted and at worst be incorrect. Paramount among these is the idea that the inductive effect of π-(phenyl)chromium tricarbonyl may be approximated by that of *p*-nitrophenyl. This suggestion is not original with us but stems from the observation that [π-(phenyl)chromium tricarbonyl]acetic and *p*-nitrophenylacetic acids have experimentally identical ionization constants in 50% ethanol at 25°.[22] However, the geometries of these two aryl groups are obviously quite different and the individual bond moments in each must clearly be oriented in different directions with respect to the remainder of the molecule. Hence, it is the time-averaged net moment of all possible conformations which must be similar in 50% ethanol. The relative population of the various conformers of a polar molecule is known to be solvent dependent,[29] so that the *p*-nitrophenyl may not be a good model for the conformationally averaged net inductive effect of the π-complexed phenyl in other solvents, especially when their dipole moments differ as much as those of acetic (D = 6) and formic acids (D = 58). While we recognize the possible pitfalls of the assumption, in the absence of something better we see no recourse but to continue to use it.

Another possibility may be that the ability of the tricarbonylchromium to act as a source of electrons is diminished by protonation in the more acidic formic acid (pK_a = 3.75). Both Wilkinson, *et al.*,[30] and Sahatjian[31] have demonstrated by nmr that π-arenechromium tricarbonyl complexes are extensively protonated on chromium in trifluoroacetic acid. Clearly to the extent that such protonation occurs during solvolysis, the effective concentration of the more reactive unprotonated starting material will be reduced. Although we have been unable to detect any high-field resonance in the 60-MHz nmr spectrum of a solution of 2-OAc in unbuffered formic acid, we cannot completely discount metal protonation as a possible source of the reduced participation observed in this solvent.

While it is possible that the slightly reduced apparent participation by π-phenylchromium tricarbonyl in formolysis relative to acetolysis may be an artifact of our interpretation, other β-arylalkyl groups *do* exhibit the same phenomena in systems such as β-arylethyl and neophyl, where the leaving group is attached to a primary carbon. As the data in Table VI illustrate, the increase in solvolysis rate which accompanies a solvent change from acetic to formic acid is always greater under comparable conditions for the unsubstituted phenyl derivative than for the comparable *p*-methoxy compound. In other words, in highly solvated primary systems[32] the effectiveness of *p*-anisyl as a neighboring group is decreased relative to phenyl when the solvent itself can provide more electrophilic stabilization. As a similar reactivity pattern prevails for π-phenylchromium tricarbonyl relative to phenyl, it is perhaps not surprising that in the primary sulfonate esters examined here the apparent additional anchimeric effect re-

(28) This conclusion is corroborated by the finding, reported elsewhere [R. S. Bly and R. C. Strickland, *J. Amer. Chem. Soc.*, **92**, 7459 (1970)], that under kinetically controlled conditions the acetolysis of both *exo*-2-[π-*exo*- and -*endo*-(benzonorbornenyl)chromium tricarbonyl] methanesulfonates yields the less stable, more hindered *exo*-[π-*endo*-(benzonorbornenyl)-chromium tricarbonyl] acetate preferentially.

(29) *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 159–160, and references cited therein.

(30) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.* 3653 (1962).

(31) R. A. Sahatjian, Ph.D. dissertation, University of Massachusetts, 1969.

(32) Primary cations are far too unstable to exist in solution;[9d] *cf.* S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951); M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968). In fact it has been suggested that in such primary systems the rate-limiting step may actually be the dissociation of a tight ion pair;[2a] *cf.* R. A. Sneen and J. W. Larson, *ibid.*, **91**, 6031 (1969); V. J. Shiner, Jr., and W. Dowd, *ibid.*, **91**, 6528 (1969); J. M. Scott, *Can. J. Chem.*, **48**, 3807 (1970).

Table VI
Effect of Solvent on the Extent of Aryl Participation in Primary β-Arylalkyl Sulfonate Esters

Compd	Temp, °C	Fk_Δ, sec^{-1} HCOOH	Fk_Δ, sec^{-1} HOAc	HCOOH/HOAc
β-Phenylethyl tosylate (1-OTs)	74	2.64×10^{-5} [a]	6.88×10^{-8} [b]	384
β-p-Anisylethyl tosylate	74	1.61×10^{-3} [c]	8.78×10^{-6} [b]	183
β-Phenylethyl methanesulfonate (1-OMs)	90	9.93×10^{-5} [d]	4.4×10^{-7} [d]	~225
π-β-Phenylethyl methanesulfonate (2-OMs)	90	1.11×10^{-3} [d]	5.6×10^{-6} [d]	~198
2-Phenyl-1-propyl methanesulfonate (*dl*-5-OMs)	90	1.27×10^{-3} [d]	1.67×10^{-5} [d]	76
π-2-Phenyl-1-propyl methanesulfonate (*dl*-6-OMs)	90	3.00×10^{-3} [d]	5.4×10^{-5} [d]	56
2-Phenyl-2-methyl-1-propyl tosylate	25	1.16×10^{-5} [e]	3.11×10^{-8} [f]	374
2-p-Anisyl-2-methyl-1-propyl tosylate	25	8.31×10^{-4} [g]	6.00×10^{-6} [f]	139

[a] Reference 13c. [b] Calculated from the data in ref 12b. [c] Interpolated from the data of ref 3b and W. H. Saunders, Jr., and R. Glaser, *J. Amer. Chem. Soc.*, **82**, 3586 (1960), assuming $Fk_\Delta \approx k_t$ in this solvent. [d] This work. [e] Data of A. H. Fainberg quoted by R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3278 (1957), assuming $Fk_\Delta \approx k_t$. [f] Extrapolated from the data in ref 12b assuming $Fk_\Delta \approx k_t$. [g] S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956).

sulting from π complexation prior to solvolysis is less in formic than in acetic acid.[33]

Experimental Section[34]

Preparation of the Methanesulfonates (1-, 3-, *dl*-5-, 7-, and *dl*-8-OMs).—The methanesulfonates were prepared by the reaction of methanesulfonyl chloride in pyridine with the corresponding alcohols 1-OH,[35] 3-OH,[36] *dl*-5-OH,[14,37] 7-OH,[38] and *dl*-8-OH[39] as described previously.[2a] Melting points and yields are listed in Table VII.

Table VII
Melting Points and Yields of the 2-Arylethyl and 2-Arylpropyl Methanesulfonates

Compd	Mp, °C	Yield, %
1-OMs	Liquid at room temperature	61
3-OMs	Liquid at room temperature	56
dl-5-OMs	Liquid at room temperature	60
7-OMs	80–81	41
dl-8-OMs	85–86	27

2-Phenylethyl Methanesulfonate (1-OMs).—Ir analysis showed ($CHCl_3$) 3070, 3060, 3020 (CH phenyl); 2960, 2930 (CH aliphatic); 1610, 1590 (aromatic nucleus); 1350, 1165 (OSO_2); and 699 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) δ 7.25, singlet (C_6H_5); 4.36, triplet, J = 7.0 Hz ($-CH_2CH_2O$); 3.01, triplet, J = 7.0 Hz ($C_6H_5CH_2CH_2-$); and 2.78, singlet ($-OSO_2CH_3$).

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.97; H, 6.04; O, 23.97; S, 16.01. Found: C, 54.08; H, 6.20; O, 23.91; S, 15.86.

2-Phenylethyl-*1,1-d*$_2$ Methanesulfonate (3-OMs).—Ir analysis showed ($CHCl_3$) 3030 (CH phenyl); 2940 (CH aliphatic); 2250, 2170 (CD aliphatic); 1610, 1590 (aromatic nucleus); 1370, 1178 (OSO_2); 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) δ 7.19, singlet (C_6H_5); 2.95, singlet ($C_6H_5CH_2-$); 2.75, singlet (OSO_2CH_3).

2-Phenyl-1-propyl Methanesulfonate (*dl*-5-OMs).—Ir analysis showed (CCl_4) 3080, 3060, 3025 (CH phenyl); 2960, 2935, 2895, 2875 (CH aliphatic); 1610, 1590 (aromatic nucleus); 1355, 1175 (OSO_2); 700 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.12, singlet (C_6H_5-); 4.10, doublet, J = 7.0 Hz ($>CHCH_2O-$); 3.08, multiplet [$C_6H_5CH(CH_3)CH_2-$]; 2.65, singlet (OSO_2CH_3); 1.29, doublet, J = 7.0 Hz ($>CHCH_3$).

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59; O, 22.40; S, 14.96. Found: C, 55.91; H, 6.75; S, 15.14.

2-(*p*-Nitrophenyl)ethyl Methanesulfonate (7-OMs).—Ir analysis showed ($CHCl_3$) 3040 (CH aromatic); 2980, 2920, 2880, 2820 (CH aliphatic); 1530, 1370, 1350 (CNO_2, OSO_2), 1170 (OSO_2); 850 cm^{-1} (disubstituted phenyl); nmr ($CDCl_3$) δ 8.28, 8.13, 7.54, 7.39, AB quartet, J = 8 Hz ($-C_6H_2^AH_2^B-$); 4.54, triplet, J = 6.5 Hz ($-CH_2CH_2O-$); 3.25 ,triplet, J = 6.5 Hz ($-C_6H_4-CH_2CH_2-$); 3.04, singlet ($-OSO_2CH_3$).

Anal. Calcd for $C_9H_{11}NO_5S$: C, 44.07; H, 4.52; N, 5.71; O, 32.62; S, 13.07. Found: C, 44.06; H, 4.62; N, 5.59; S, 13.13.

2-(*p*-Nitrophenyl)-1-propyl Methanesulfonate (*dl*-8-OMs).—Ir analysis showed ($CHCl_3$) 3060, 3020 (CH phenyl); 2970, 2930 (CH aliphatic); 1350, 1170 (OSO_2); 855 cm^{-1} (phenyl); nmr (acetone-d_6) δ 8.16, 8.01, 7.57, 7.42, AB quartet, J = 8 Hz ($-C_6H_2^AH_2^B-$); 4.34, doublet, J = 6.5 Hz ($>CHCH_2O-$); 3.35, multiplet ($-CHCH_3CH_2-$); 2.98, singlet ($-OSO_2CH_3$); 1.35, doublet, J = 6.5 Hz ($>CHCH_3$).

Anal. Calcd for $C_{10}H_{13}NO_5S$: C, 46.32; H, 5.05; N, 5.40; O, 30.86; S, 12.37. Found: C, 46.32; H, 5.15; N, 5.27; O, 30.91; S, 12.36.

Preparation of the π-Complexed Methanesulfonates (2-, 4-, and *dl*-6-OMs).—The methanesulfonates 2-, 4-, and *dl*-6-OMs were prepared by the reaction of chromium hexacarbonyl with the corresponding noncomplexed methanesulfonates, 1-OMs, 3-OMs, and *dl*-5-OMs, respectively, as described previously.[2a] The yields and melting points are summarized in Table VIII.

Table VIII
Melting Points and Yields of the π-Complexed 2-Phenylethyl and 2-Phenyl-1-propyl Methanesulfonates

Compd	Mp, °C	Yield, %
2-OMs	70–71	97
4-OMs	70–71	54[a]
dl-6-OMs	49.5–50.5	68

[a] The low yield is probably due to the reduced scale of this preparation.

2-[π-(Phenyl)chromium tricarbonyl]ethyl Methanesulfonate (2-OMs).—Ir analysis showed ($CHCl_3$) 3030 (CH phenyl); 2970, 2940 (CH aliphatic); 1980, 1910 (C≡O); 1380, 1170 (OSO_2); 660, 633, 530 cm^{-1} (CrC);[40] nmr ($CDCl_3$) δ 5.35, doublet (π-C_6H_5-); 4.43, triplet, J = 6.5 Hz ($-CH_2CH_2O-$); 3.03, singlet

(33) It is interesting to note that in the 1-aryl-2-propyl tosylate series, where the incipient cations are secondary and thus intrinsically more stable and less highly solvated in the transition state, these effects are reversed, *viz.*, the better neighboring group *p*-anisyl provides relatively more additional internal nucleophilic assistance than phenyl when the solvent is changed from acetic to formic acid.[9c]

(34) Melting points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalitisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrometer, Model 337, a Model 202 ultraviolet spectrometer, and a Varian A-60A nmr spectrometer. Gas chromatographic analyses were performed on a F & M Model 500 chromatograph equipped with a 16 ft × 0.5 in. column packed with 20% Carbowax 20M on 60–80 mesh Gas-Chrom CL. Helium was used as carrier gas at flow rates of 80–100 ml/min. The potentiometric titrations were performed on a Radiometer Auto-Burette using glass and standard calomel electrodes.

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($-OSO_2CH_3$); 2.85, triplet, $J \cong 6.5$ Hz ($C_6H_5CH_2CH_2-$); uv (C_2H_5OH) 218 mμ (ε 22,000), 254 (6000), 317 (7900).[41]

Anal. Calcd for $C_{12}H_{12}O_6SCr$: C, 42.86; H, 3.60; O, 28.55; S, 9.54; Cr, 15.46. Found: C, 42.81; H, 3.67; O, 28.12; S, 9.32.

2-[π-(Phenyl)chromium tricarbonyl]ethyl-1,1-d_2 Methanesulfonate (4-OMs).—Ir analysis showed ($CHCl_3$) 3080, 3020 (CH phenyl); 2930 (CH aliphatic); 2250, 2170 (CD aliphatic); 1970, 1880 (C≡O); 1340, 1170 (OSO_2); 655, 629 cm^{-1} (CrC).

Anal. Calcd for $C_{12}H_{10}D_2O_6SCr$: C, 42.61; H, 2.98; D, 1.18; O, 28.38; S, 9.48; Cr, 15.37. Found: C, 42.75; O, 28.30; S, 9.37.

2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonate (*dl*-6-OMs).—Ir analysis showed (CCl_4) 3030, w (*CH* phenyl); 2980, w (CH aliphatic); 1980, 1920 (C≡O); 1390, 1178 (OSO_2); 660, 630 cm^{-1} (CrC); nmr ($CDCl_3$) δ 5.08, singlet (π-C_6H_5–); 3.99, doublet, $J = 6$ Hz (>$CHCH_2O$–); 2.74, singlet ($-OSO_2CH_3$) superimposed on a multiplet at ~2.7 ($C_6H_5CHCH_3CH_2$–); 1.10, doublet, $J = 7.5$ Hz (>$CHCH_3$).

Anal. Calcd for $C_{13}H_{14}O_6SCr$: C, 44.57; H, 4.03; O, 27.40; S, 9.15; Cr, 14.84. Found: C, 44.68; H, 4.11; O, 27.24; S, 9.36.

Acetolysis rates were measured titrimetrically in sodium acetate buffered, deoxygenated anhydrous acetic acid[42] as described previously.[2a] The rate constants and activation parameters are recorded in Table I.

Formolysis Rates.—Anhydrous formic acid was obtained by purification of the commercial solvent (Baker and Adams CP, 98–100%) according to the procedure of Winstein.[3a] Sodium formate was dried at 120° overnight and added to the purified solvent to obtain a ~0.03 *M* solution. The buffered solution was deoxygenated as described previously for the acetic acid solvent.[2a]

The rates were measured using the ampoule technique. Enough of the methanesulfonate was dissolved in 25 ml of the buffered formic acid to obtain an ~0.02 *M* solution. Eight 3-ml samples were placed into ampoules, cooled in Dry Ice–acetone, flushed with dry nitrogen, sealed, and placed in a thermostated bath. At appropriate intervals ampoules were removed from the bath, cooled, and opened, and 2-ml aliquots were withdrawn. The measured volume was diluted with 20 ml of anhydrous acetic acid and titrated potentiometrically[34] with a standard solution of ~0.033 *M* perchloric acid in acetic acid.

Acetolysis Products of 2-Phenylethyl Methanesulfonate (1-OMs). Run A.—A 10-ml sample of a 0.02 *M* solution of 1-OMs in anhydrous acetic acid[42] buffered with 0.046 *M* sodium acetate was allowed to react at 115° for 84 hr (10 half-lives). The solution was cooled, poured over cracked ice, and extracted with three 25-ml portions of pentane. The combined extract was washed with saturated sodium bicarbonate, then washed with water and dried over anhydrous sodium sulfate. The solution was filtered and concentrated to ~2 ml by slow distillation of the pentane through a 12-in. wire spiral packed vacuum-jacketed column. Analysis by glpc at 140° showed the presence of two components whose relative retention times and (peak areas) were 4.1 (<0.1%) and 29.4 (>99.9%). No attempt was made to identify the first component. The second component was identical with the known and commercially available 2-phenylethyl acetate (1-OAc).[43]

Acetolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-ethyl Methanesulfonate (2-OMs). Run B.—A solution of 33 mg (0.099 mmol) of the methanesulfonate in 5 ml of deoxygenated acetic acid[2a] buffered with 0.046 *M* sodium acetate was heated at 115° for 8.4 hr (10 half-lives). The solution was cooled, poured over cracked ice, and extracted with three 50-ml portions of a 1:1 pentane–ether mixture. The extract was washed successively with cold saturated sodium bicarbonate and cold water. To the washed extract was added dropwise with rapid stirring a solution of ceric ammonium nitrate in acetone.[44] The resulting colorless solution was washed with cold water, dried (Na_2SO_4), and treated with an excess of lithium aluminum hydride.[2a] Analysis of the reduced product solution by glpc on the 16-ft Carbowax column revealed the presence of three components with relative retention times (peak areas) of 10.4 (<0.1%), 19.0 (<0.1%), and 22.5 (>99%). The first two components were not isolated and characterized. The third component was identical in all respects with authentic 2-phenylethanol (1-OH).[35] A duplicate run C gave identical results.

Acetolysis of 2-[π-(Phenyl)chromium tricarbonyl]ethyl-1,1-d_2 Methanesulfonate (4-OMs). Run D.—This reaction was carried out in the same manner as run B except that the lithium aluminum hydride reduction step was omitted. The acetate product(s), isolated by glpc, showed ir (CCl_4) peaks at 3090, 3070, 3040 (CH phenyl); 2950 (CH aliphatic), 2260, 2180 (CD aliphatic); 1760 (C=O ester); 1610, 1590 (phenyl nucleus); 1028 (CO ester); 721, 700 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.18, singlet (C_6H_5–); 2.87, singlet ($C_6H_5CH_2$–); 1.95, singlet ($-COCH_3$). No signals were observed at δ ~4.3 ($-CH_2O$–). We estimate that ~3% of α-hydrogen-containing material could have been detected had it been present. The acetate isolated in a duplicate run E also contained <3% of hydrogen at the α position.

π-Complexed Products from the Acetolysis of 2-[π-(Phenyl)-chromium tricarbonyl]ethyl Methanesulfonate (2-OMs). Run F.—To 50 ml of 0.0487 *M* sodium acetate in deoxygenated acetic acid[2a] was added 0.650 g (1.92 mmol) of 2-OMs. The sample was sealed under nitrogen and heated at 115° in the dark for 11 hr (13 half-lives). The solution was poured over ~200 ml of cracked ice and then extracted as described for run B. The extract was dried ($MgSO_4$) and filtered. Addition of pentane to the filtrate caused the precipitation of 0.332 g (57.4%) of yellow crystals, mp 51–52°. Ir analysis showed ($CHCl_3$) 3020 (CH phenyl), 2960 (CH aliphatic); 1970, 1880 (C≡O); 1735 (C=O ester); 660, 630, 530 cm^{-1} (CrC); nmr ($CDCl_3$) δ 5.33, singlet (π-C_6H_5–); 4.32, triplet, $J = 6$ Hz ($-CH_2CH_2O$–); 2.77, triplet, $J = 6$ Hz ($C_6H_5CH_2CH_2$–); 2.16, singlet (CH_3CO_2–).

Anal. Calcd for $C_{13}H_{12}O_5Cr$: C, 52.00; H, 4.03; O, 26.65; Cr, 17.32. Found: C, 52.11; H, 4.10; O, 26.52.

The pale yellow mother liquor was treated with ceric ammonium nitrate (see run B) and analyzed by glpc on the 16-ft Carbowax column. A single component was observed. The product, isolated by glpc, was found to be identical with authentic 1-OAc.

Acetolysis Products of 2-Phenyl-1-propyl Methanesulfonate (*dl*-5-OMs). Run G.—To 50 ml of 0.0486 *M* sodium acetate in acetic acid was added 0.43 g (2.02 mmol) of the methanesulfonate. The solution was heated at 115° for 22 hr (~24 half-lives) and the product(s) were extracted and reduced with lithium aluminum hydride as described for run B. Analysis by glpc at 155° revealed the presence of five components whose relative retention times (peak areas) were 4.0 (8.7%), 5.3 (6.0%), 7.1 (14.5%), 34.8 (70.8%), and 42.0 (trace). The first, second, third, and fourth components were found to be identical with the known and commercially available[45] compounds allylbenzene (**10**), *cis*-β-methylstyrene (**11**), *trans*-β-methylstyrene (**12**), and 1-phenyl-2-propanol (*dl*-**13**-OH), respectively. The fifth component was not present in sufficient amounts for isolation and identification.

Acetolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonate (*dl*-6-OMs). Run H.—The reaction was carried out at 115° for 4 hr (~15 half lives) as described for run B. A glpc analysis of the decomplexed and reduced product mixture showed two components in a relative abundance of 5.1 and 94.9% which were identified by spectral comparison as alcohols *dl*-**13**-OH and *dl*-**5**-OH, respectively.

Formolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-ethyl Methanesulfonate (2-OMs). Run I.—To 50 ml of a solution of 0.0491 *M* sodium formate in deoxygenated formic acid (>97%, Matheson Coleman and Bell) was added 0.686 g (2.04 mmol) of 2-OMs. The solution was heated in a sealed ampoule in the dark at 115° for 1 hr, cooled, poured over cracked ice, and extracted with three 100-ml portions of a 1:1 ether–pentane mixture. The extract was washed with sodium carbonate, then with water, and concentrated to ~40 ml. Addition of ~100 ml of pentane to the concentrate gave 0.413 g (71%) of a yellow, crystalline product (2-OCOH): mp 71–72°; ir ($CHCl_3$) 3080, 3020 (CH phenyl); 2950, 2930, 2890 (CH aliphatic); 1950, 1870 (C≡O); 1735 (C=O ester); 658, 630, and 530 cm^{-1} (CCr); nmr ($CDCl_3$) δ 8.06, singlet (–OCOH); 5.60, broad singlet (π-C_6H_5–); 4.41, triplet, $J = 6$ Hz ($-CH_2CH_2O$–); 2.79, triplet, $J = 6$ Hz ($C_6H_5CH_2CH_2$–).

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Anal. Calcd for $C_{12}H_{10}O_5Cr$: C, 50.35; H, 3.52; O, 27.95; Cr, 18.18. Found: C, 50.51; H, 3.56; O, 27.75.

The filtrate was further concentrated to ~20 ml and treated with ceric ammonium nitrate followed by lithium aluminum hydride as described for run B. Glpc analysis showed a single product, identical with authentic 1-OH.

Run J.—Another sample (0.684 g, 2.03 mmol) of the methanesulfonate 2-OMs was treated in a similar manner with anhydrous buffered formic acid at 70° for 30 min. The product was isolated as described for run I, giving 0.405 g (70%) of 2-OCOH.

Formolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-ethyl-1,1-d_2 Methanesulfonate (4-OMs). Run K.—A solution of 0.355 g (1.05 mmol) of 4-OMs in 25 ml of deoxygenated formic acid[2a] buffered with 0.0491 *M* sodium formate was heated at 120° for 1 hr. The complexed formate 4-OCOH (0.209 g, 69%) was isolated as described in run I: mp 71–72°; ir ($CHCl_3$) 3090, 3035 (CH phenyl); 2980, 2945, 2920 (CH aliphatic); 2170 (CD aliphatic); 1980, 1890 (C≡O), 1730 (C=O ester), 1190 (CO); 660, 630 cm^{-1} (CrC); nmr ($CDCl_3$) δ 8.02, singlet (-OCOH); 5.30, broad singlet (π-C_6H_5-); 2.75, singlet ($C_6H_5CH_2$-). No signals were observed at δ ~4.4 (-CH_2O-). We estimate that ~5% of α-hydrogen-containing material could have been detected had it been present.

Anal. Calcd for $C_{12}H_8D_2O_5Cr$: C, 50.01; H, 2.80; D, 1.39; O, 27.76; Cr, 18.04. Found: C, 50.28; O, 27.70.

Formolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-1-propyl Methanesulfonate (*dl*-6-OMs). Run L.—A solution of 61.8 mg (0.176 mmol) of *dl*-6-OMs in 5 ml of deoxygenated formic acid[2a] was heated at 115° for 30 min. The reaction mixture was extracted, decomplexed with ceric ammonium nitrate, reduced with lithium aluminum hydride, and analyzed by glpc as described for run B. Two components were found to be present (relative abundance 17% and 83%) which were identified by their infrared spectra as alcohols *dl*-13-OH and *dl*-5-OH, respectively.

Registry No.—1-OMs, 20020-27-3; 2-OCOH, 38599-99-4; 2-OAc, 38600-00-9; 2-OMs, 38600-01-0; 3-OMs, 38605-70-8; 4-OMs, 38600-02-1; 4-OCOH, 38600-03-2; (±)-5-OMs, 38605-48-0; (±)-6-OMs, 38600-04-3; 7-OMs, 20020-28-4; (±)-8-OMs, 38637-45-5.

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Kinetics of the Acid-Catalyzed Closure of Hydantoic Acids. Effect of 2-Aryl and 2-Alkyl Substituents[1]

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Ring closure of hydantoic acids to hydantoins studied under aqueous acid conditions in the pH range 0–2 at 50° shows a specific acid-catalyzed component at low pH as well as a spontaneous component at higher pH. The accelerating effect of substitution on the 2 carbon of hydantoic acids by alkyl or aryl groups is not always as large as can be expected on the basis of their bulk. The observed rates appear to be rationalizable, however, in terms of a competing acceleration–inhibition mechanism resulting from the substituents being able to interfere with the reaction center as well as assisting in the process.

Hydantoic acids are known to cyclize to their respective hydantoin under acid conditions and the effects of 2 substituents has been qualitatively observed.[2] The only data available for the attack of a ureido group at a carboxyl group are the kinetics of the acid-catalyzed closure of a para-substituted phenylthiocarbamoylleucine, but the closure resulted in a thiohydantoin.[3] More recently, Projarlieff, *et al.*,[4,5] have reported studies on the acid-catalyzed reversible cyclization of ureidopropionic acid to yield dihydrouracil which, although not a hydantoin, possesses chemical characteristics similar to hydantoins. Bruice, *et al.*, studied quantitatively the conversion of *O*-ureidobenzoic acid and its esters to 2,4-(1*H*,3*H*)-quinazolinedione, a hydantoin-like molecule, under basic conditions.[6,7] The effects of alkyl and aryl substituents in intramolecular closures has been well documented, with the results suggesting that, as the bulkiness of substituents in cyclization reactions was increased, the rates of cyclization increased.[8–20] However, exceptions to this rule do exist.[16,19]

Despite the large amount of work done on hydantoins, the kinetics of the acid-catalyzed cyclization of hydantoic acids and the effects of 2 substituents have not been quantitated. In the present study the kinetics of the cyclization and the effect of 2 substituents on the

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