C, 75.34; H, 8.71. Found: C, 74.66; H, 8.99.

The component of low R_f was eluted with ethyl acetate; reduction in volume of the resulting solution gave 65 mg (32%) of **37**: mp 59–60 °C; ^{1}H NMR (CCl_4) δ 0.96 (br t, $J \simeq 6$ Hz, 3 H, terminal CH_3 of hexadecyl chain), 1.33 (br s, 28 H, interior methylenes of hexadecyl chain), 2.90 (br s, 4 H, Ar—$(CH_2)_2$—pyr), 3.47 (s, 3 H, NCH_3), 4.16 (br t, J = 6 Hz, 2 H, CO_2CH_2), 5.86 (d, J = 8 Hz, 1 H, H-5 of pyridone ring), 7.23 (br s, 9 H, Ar H of Ar—S—Ar), 7.80 (d, J = 8 Hz, 1 H, H-4 of pyridone ring); UV (CH_2Cl_2) λ_{max} 245 nm (ϵ 7600), 273, 345 (6300). Anal. ($C_{37}H_{51}NO_3S$) C, H.

6-[(4′-Phenylthio)-(*E*)-styryl]-2-pyridone-3-carboxylic Acid (39). The LDA dilithiation of 4.57 g (27.3 mmol) of carboxylic acid **38** was performed in a manner analogous to that employed for the preparation of **34**. The dilithiated species was then trapped by addition at −78 °C of a THF solution of 5.86 g (27.3 mmol) of 4-(phenylthio)benzaldehyde.[24,47] The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After the mixture was quenched with a few drops of water and acidified to pH 3 with 10% aqueous HCl, extractive workup provided a yellow solid which was indicated by ^{1}H NMR to be composed of 85% of the desired secondary carbinol. This material was not purified but was, instead, dehydrated directly by heating with 6.0 g (31.5 mmol) of toluenesulfonic acid monohydrate in toluene at reflux with continuous removal of the water formed. The orange solid obtained was taken up in hot glacial acetic acid and decolorized with carbon. The solids obtained on cooling were washed with water followed by recrystallization of the crude material from glacial acetic acid to give 2-pyridone **39**. The yield of yellow plates, mp 270–271 °C dec, was 7.1 g (74% overall from **38**): ^{1}H NMR (Me_2SO-d_6) δ 6.95 (d, J = 8.4 Hz, 1 H, pyridone H-5), 7.05 (d, J = 15.6 Hz, 1 H, olefinic proton α to pyridone ring), 7.40 (AA′BB′ q, J = 8.4 Hz, 4 H, disubstituted Ar H), 7.40 (s, 5 H, 5 Ar H), 7.78 (d, J = 15.6 Hz, 1 H, olefinic H α to phenyl ring), 8.30 (d, J = 8.4 Hz, 1 H, pyridone H-4); IR (Nujol mull) 3400–2400 (br, COOH OH), 1742 (COOH C=O), 1632 (lactam C=O), 973 (trans olefinic CH deformation); mass spectrum (70 eV), m/e (% of base) 351 (8.61), 350 (24.76), 349 (M^+, 100). Anal. ($C_{20}H_{15}NO_3S$) C, H, N, S.

(47) H. H. Szmant, J. M. Segedi, and J. Dudek, *J. Org. Chem.*, 18, 745–7 (1953).

***n*-Hexadecyl 6-[(4′-Phenylthio)-(*E*)-styryl]-2-pyridone-3-carboxylate (13).** Esterification of 4.80 g (13.7 mmol) of **39** was accomplished by alkylation of the corresponding tetramethylammonium salt with 5.74 g (14.4 mmol) of hexadecyl tosylate in HMPA in a manner analogous to that employed for the corresponding saturated system **35**. The crude product so obtained was purified by medium-pressure LC on silica gel employing 70/25/5 chloroform/hexane/ethyl acetate as the mobile phase. The fractions containing **13** were combined, and the solvent was removed at reduced pressure. The resulting yellow solid was crystallized from hexane to afford 4.00 g (51%) of pure **13** as bright yellow, matted needles: mp 135–136 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (br t, $J \simeq 6$ Hz, 3 H, terminal CH_3 of hexadecyl chain), 2.29 (br s, 38 H, interior methylenes of hexadecyl chain), 4.27 (t, J = 6 Hz, 2 H, CO_2CH_2), 6.57 (d, J = 8.4 Hz, 1 H, pyridone H-5), 6.86 (d, J = 15.4 Hz, 1 H, CH=$CHC_6H_4C_6H_5$), 7.10–7.73 (m, 9 H, Ar H of Ar—S—Ar), 7.85 (d, J = 15.4 Hz, 1 H, CH=$CHC_6H_4SC_6H_5$), 8.13 (d, J = 8.4 Hz, 1 H, pyridone H-4); IR (Nujol mull) 1751, 1736 (ester C=O), 1631 (lactam C=O), 1282, 1149 (ester CO), 989 cm^{-1} (trans olefinic CH deformation); UV (cyclohexane) λ_{max} 219 nm (ϵ 15 500), 254 (14 400), 373 (35 300); mass spectrum (70 eV), m/e (% of base) 575 (17), 574 (40.3), 573 (M^+, 100), 332 (64.7). Anal. ($C_{36}H_{47}NO_3S$) C, H, N, S.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

Registry No. 1, 72762-00-6; **2**, 142-08-5; **3**, 73018-09-4; **4**, 17228-61-4; **5**, 72917-96-5; **6**, 72982-87-7; **7**, 72917-97-6; **8**, 73035-73-1; **9**, 72917-98-7; **10**, 72983-37-0; **11**, 72917-99-8; **12**, 73035-74-2; **13**, 72918-00-4; **14**, 73035-75-3; **15**, 73018-10-7; **16**, 2637-34-5; **17**, 626-64-2; **18**, 108-96-3; **19**, 17368-12-6; **20**, 17228-67-0; **21**, 13603-44-6; **22**, 7516-31-6; **23**, 72918-01-5; **24**, 72918-02-6; **26**, 4241-27-4; **27**, 72918-03-7; **28**, 72918-04-8; **29**, 72918-05-9; **30a**, 72918-06-0; **30b**, 72918-07-1; **31**, 72918-08-2; **32**, 72918-09-3; **33**, 72918-10-6; **34**, 72918-11-7; **35**, 72918-12-8; **36**, 72918-13-9; **37**, 72918-14-0; **38**, 38116-61-9; **39**, 72918-15-1; 4-hydroxy-6-methyl-2-pyridone, 3749-51-7; 2,4-dimethoxy-6-methylpyridine, 40334-96-1; 2-methoxy-1,6-dimethyl-4-pyridone, 40334-98-3; 2-ethoxy-3-cyano-6-methylpyridine, 54957-81-2; 4-(phenylthio)benzyl chloride, 1208-87-3; 1,2-bis[4-(phenylthio)-phenyl]ethane, 72918-16-2; *n*-hexadecyl tosylate, 6068-28-6; 4-(phenylthio)benzaldehyde, 1208-88-4.

π-Complexed β-Arylalkyl Derivatives. 6. Effect of Electron-Withdrawing Substituents on the Acetolysis of 2-[π-(Aryl)chromium tricarbonyl]-2-methyl-1-propyl Methanesulfonates[1]

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The π-(arene)chromium tricarbonyl complexes of *m*-methoxy- and *p*-chloro-substituted 2-[π-(phenyl)chromium tricarbonyl]-2-methyl-1-propyl (neophyl) methanesulfonates have been prepared and their acetolysis rates determined. At 99.5 °C, the complexes are, respectively, 1.1 and 1.6 times as reactive as their noncomplexed counterparts. The *p*-chloroneophyl complex yields, after oxidative decomplexation of the product mixture with Ce(IV), 54% 3-(*p*-chlorophenyl)-2-methyl-2-propyl acetate, 34% 3-(*p*-chlorophenyl)-2-methyl-1-propene, and 12% 1-(*p*-chlorophenyl)-2-methyl-1-propene. No nonaryl-migrated products are observed. The acetolysis rates of *p*-methoxy-, *m*-methoxy-, *p*-methyl-, *m*-methyl-, and *p*-chloroneophyl complexed and noncomplexed methanesulfonates at 99.5 °C are well correlated by the Yukawa–Tsuno relations: $\log (k/k_0)_{complex} = -3.39[\sigma + 0.47(\sigma^+ - \sigma)] - 0.03$ and $\log (k/k_0)_{noncomplex} = -1.97[\sigma + 0.18(\sigma^+ - \sigma)] - 0.16$. The meaning of these correlations is discussed, and it is concluded that in addition to its strong inductive electron withdrawal, π-tricarbonylchromium acts amphoterically to donate or withdraw electrons by resonance. From a comparison of the relative acetolysis rates of the *p*- and *m*-methoxy complexes, it is suggested that the π-tricarbonylchromium probably does not act via direct d-orbital participation to accelerate the solvolysis rates of the complexes.

In a previous paper in this series[2] we reported that the acetolysis rates at 75 °C of the π-(arene)chromium tricarbonyl complexes of 2-phenyl-2-methyl-1-propyl (neophyl) and *p*-methoxy-, *p*-methyl-, and *m*-methylneophyl

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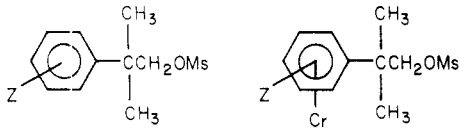
methanesulfonates, **1a**-, **2a**-, **3a**-, and **4a**-OMs, respectively,



1-OMs, Z = H
2-OMs, Z = *p*-CH_3O
3-OMs, Z = *p*-CH_3
4-OMs, Z = *m*-CH_3
5-OMs, Z = *m*-CH_3O
6-OMs, Z = *p*-Cl
7-OMs, Z = *p*-NO_2

1a-OMs, Z = H
2a-OMs, Z = *p*-CH_3O
3a-OMs, Z = *p*-CH_3
4a-OMs, Z = *m*-CH_3
5a-OMs, Z = *m*-CH_3O
6a-OMs, Z = *p*-Cl

are correlated by the relation $\log k_{complex} = -0.78\,\sigma^+ - 4.40$ while those of the noncomplexed derivatives, viz., **1**-, **2**-, **3**-, and **4**-OMs, fit the relation $\log k = -2.35\sigma^+ - 4.56$. We attributed the existence of these nonidentical linear free-energy relations of different slope (ρ) to the strong electron-withdrawing effect of the tricarbonylchromium combined with a conjugative effect which tends to suppress or "attenuate" the ability of electron-donating aryl substituents to enhance the rate of acetolysis. Using the *p*-nitro group as a model for the inductive effect of the π-tricarbonylchromium,[3] we estimated the acetolysis rates of the complexed *p*-hydro-, *p*-methoxy-, *p*-methyl-, and *m*-methylneophyl methanesulfonates to be enhanced by factors of 1600, 80, 400 and 800 times, respectively, at 75 °C. We were unable, however, to distinguish between σ–π homoconjugation and direct d-orbital participation[2] as the means by which the π-complexed moiety exerts its electron-donating effect (cf. Scheme I).

In the light of more recent studies with π-complexed benzonorbornenyl methanesulfonates[4a] and biphenylcarbinyl *p*-toluenesulfonates[5] which imply that both σ–π conjugation effects and direct d-orbital participation may be less important than dipole–charge effects in determining the acetolysis rates of such π-complex derivatives, we felt it important to extend our studies of π-tricarbonylchromium-complexed neophyl derivatives to include compounds containing electron-withdrawing substituents as well. We report here the preparation and acetolyses of the noncomplexed and complexed *p*-chloro- and *m*-methoxyneophyl methanesulfonates **5**-, **5a**-, **6**-, and **6a**-OMs, respectively.

Methods and Results

The noncomplexed methanesulfonates **5**- and **6**-OMs were prepared by known methods and converted to the desired chromium tricarbonyl complexes in a Strohmeier apparatus[6] as detailed in the Experimental Section. As expected, when the ring bears an electron-withdrawing substituent such as *p*-chloro, the complex is formed in lower yield and is less stable in solution. Acetolyses were conducted in the manner described previously.[2] The decreased reactivity of the *m*-methoxy and *p*-chloro derivatives **5a**- and **6a**-OMs, respectively, makes the use of higher temperatures obligatory and aggravates the problem of decomplexation during solvolysis.[7] Accordingly, rate constants were calculated from the slopes of first-order plots through the first 50% of reaction before extensive decomplexation had occurred. Apparent first-order titrimetric rate constants and, in the case of the *m*-methoxy π complex, activation parameters are tabulated in Table I together with the previously determined kinetic data of the other neophyl-type methanesulfonates.

The acetolysis products of the *p*-chloro complex **6a**-OMs, determined under conditions utilized for the kinetic runs

Scheme I

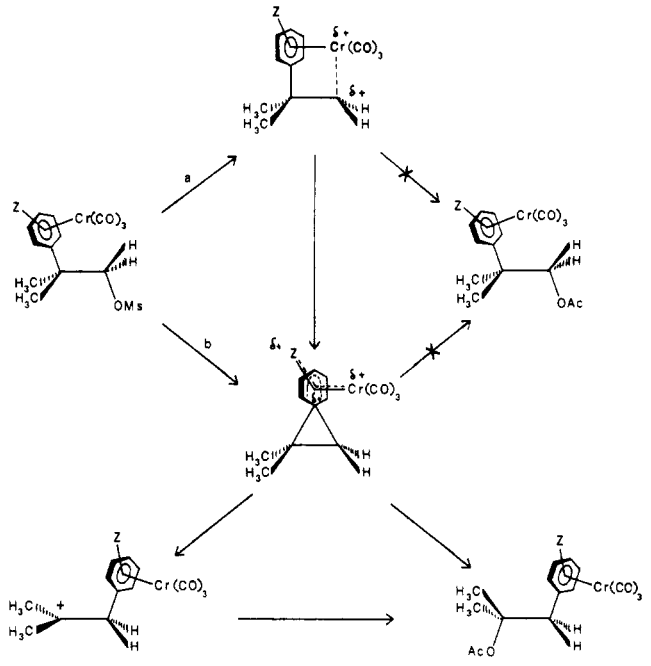


Table I. Apparent First-Order Acetolysis Constants and Activation Parameters of 2-Aryl-2-methyl-1-propyl Methanesulfonates

compd[a]	*T*, °C	10^5k, s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	k_n/k_c
1-OMs	99.5	27.8[b]	25.8	−5.96	
1a-OMs	99.5	43.5[b]	24.2	−9.28	0.64
2-OMs	99.5	1600[b]	22.6	−6.55	
2a-OMs	99.5	152[b]	23.1	−10.0	10.5
3-OMs	99.5	175[b]	24.2	−6.72	
3a-OMs	99.5	73.6[b]	23.4	−10.5	2.4
4-OMs	99.5	55.0[b]	25.1	−6.44	
4a-OMs	99.5	43.3[b]	23.6	−11.1	1.3
5-OMs[c]	99.5	14.3			
5a-OMs	99.5	16.3[b]	25.6	−7.5	0.88
	100.2	17.8 ± 0.2[d]			
	115	69.1 ± 0.9[d]			
6-OMs	99.5	6.4[e]			
6a-OMs	99.5	10.5 ± 0.4[d]			0.61
7-OMs	99.5	(0.044)[b,f]	29.0[g]	−8.0[g]	

[a] Contains 0.03–0.04 M ROMs and 0.1 M NaOAc. [b] Computed from runs at other temperatures (cf. ref 2). [c] k(5-OTs) = 16.6 × 10^{-5} s^{-1} under comparable conditions.[16] [d] Estimated error is the standard deviation of replicate determinations. [e] k(6-OTs) = 4.9 × 10^{-5} s^{-1} under comparable conditions.[15] [f] Estimated as 0.33 times the rate constant of 7-OBs.[8] [g] Reference 8.

(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, LA, Mar 1977, Abstract No. ORGN 191.
(2) R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *J. Am. Chem. Soc.*, **92**, 3722 (1970).
(3) Cf. R. S. Bly and R. L. Veazey, *J. Am. Chem. Soc.*, **91**, 4221 (1969), and references cited therein.
(4) (a) R. S. Bly and T. L. Maier, *J. Org. Chem.*, **43**, 614 (1978); (b) cf. footnote 13.
(5) R. S. Bly, K. K. Tse, and R. K. Bly, *J. Organomet. Chem.*, **117**, 35 (1976).
(6) W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).
(7) Decomplexation during acetolysis—indicated by the development of a brown-orange color in the sealed, deoxygenated tubes [Cr(II)] which changes rapidly to deep green [Cr(III)] when the tubes are opened in air—not only obscures the colorimetric end point but probably generates acetate ion in the solution, thus making the acetolysis appear slower than it actually is.[3,4b]
(8) H. Tanida, T. Tsuji, H. Ishitobi, and T. Irie, *J. Org. Chem.*, **34**, 1086 (1969).

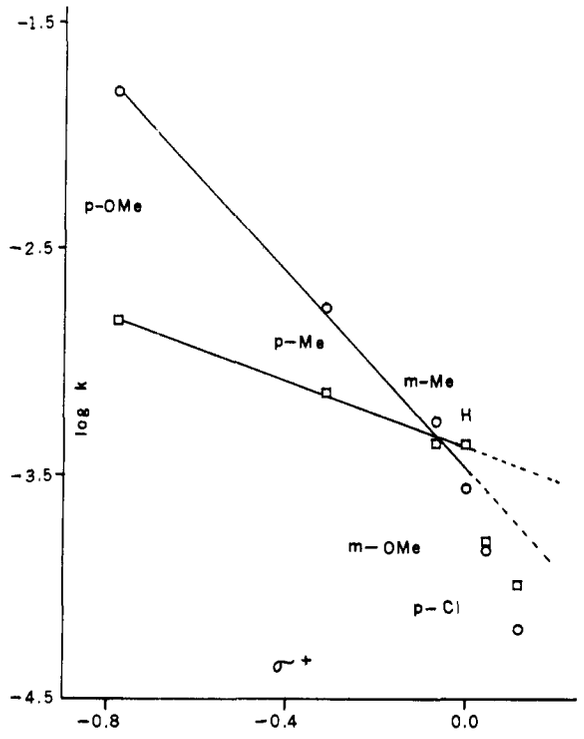
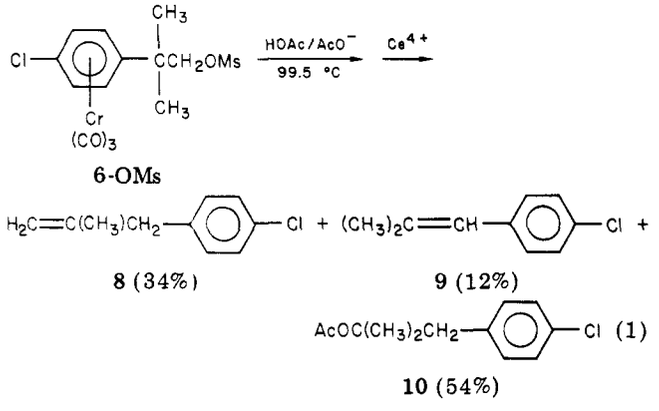


Figure 1. Acetolysis of neophyl methanesulfonates at 99.5 °C: O, noncomplexed, log $k_n = -2.18\sigma^+ - 3.47$; □, π-tricarbonylchromium complexes, log $k_c = -0.72\sigma^+ - 3.38$.

and analyzed after oxidative decomplexation with ceric ion,[2] are shown in eq 1. No unrearranged and/or methyl-migrated products were detected.



Discussion

The *m*-methoxy and *p*-chloro complexes **5a**- and **6a**-OMs solvolyze more rapidly than their noncomplexed counterparts, **5**- and **6**-OMs, but all are slower than predicted by the linear free-energy relations developed earlier for neophyl derivatives substituted with activating groups (cf. Figure 1). Apparently σ^+ overestimates the $+R$ effect of these deactivating groups. On the other hand, correlations based upon σ underestimate conjugative electron donation by strongly activating substituents such as *p*-methoxy[9] (cf. Figure 2). In such cases a linear combination of the two substituent parameters will usually give a much better correlation over a broad range of substituent effects.[10] Yukawa and Tsuno utilize eq 2 for this purpose,

$$\log (k/k_0) = \rho[\sigma + r(\sigma^+ - \sigma)] \quad (2)$$

(9) Cf. J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions", Wiley, New York, 1963, pp 211-4, and references cited therein.

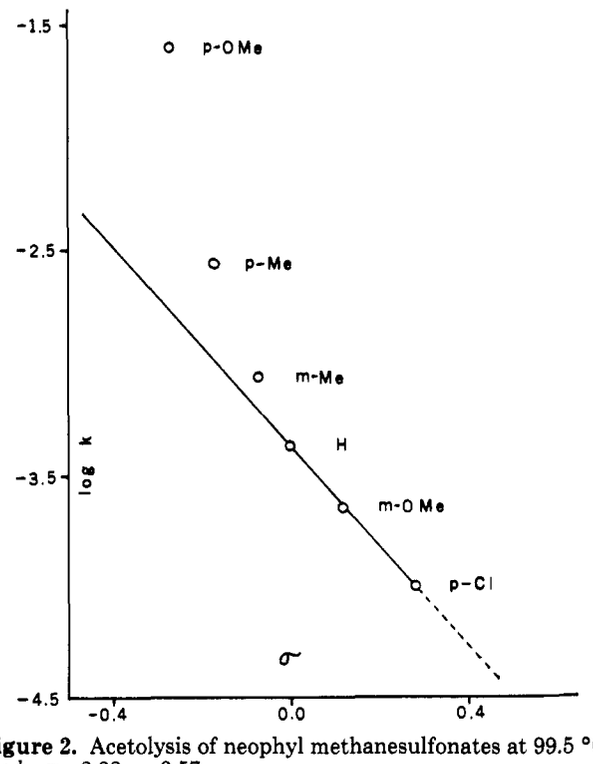


Figure 2. Acetolysis of neophyl methanesulfonates at 99.5 °C: log $k_n = -2.28\sigma - 3.57$.

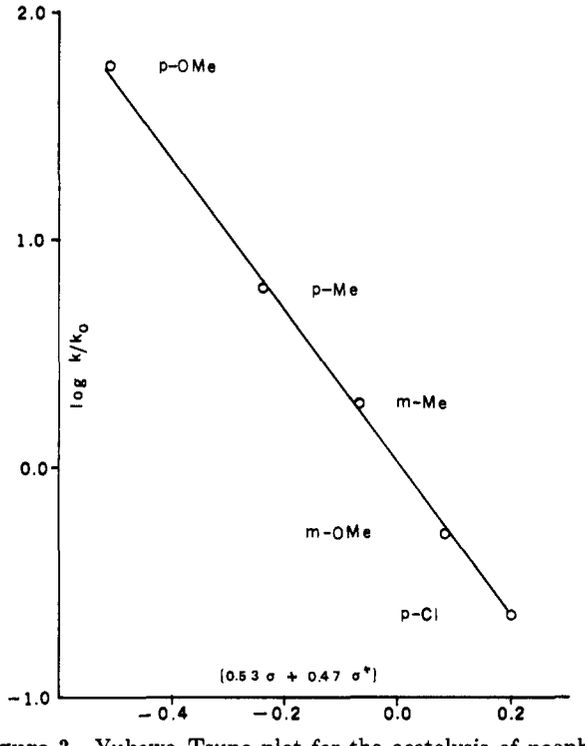


Figure 3. Yukawa-Tsuno plot for the acetolysis of neophyl methanesulfonates at 99.5 °C: log $(k/k_0) = -3.39[\sigma + 0.47(\sigma^+ - \sigma)] - 0.028$.

where r is the proportion of conjugative substituent parameter necessary to achieve the best fit.[11] Yukawa-Tsuno plots of the data in Table I are shown in Figures 3 and 4.

(10) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1972, pp 1368 ff.

(11) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **32**, 971 (1959). Note that eq 2 reduces to log $(k/k_0) = \rho\sigma^+$ when $r = 1.0$ and to log $(k/k_0) = \rho\sigma$ when $r = 0.0$.

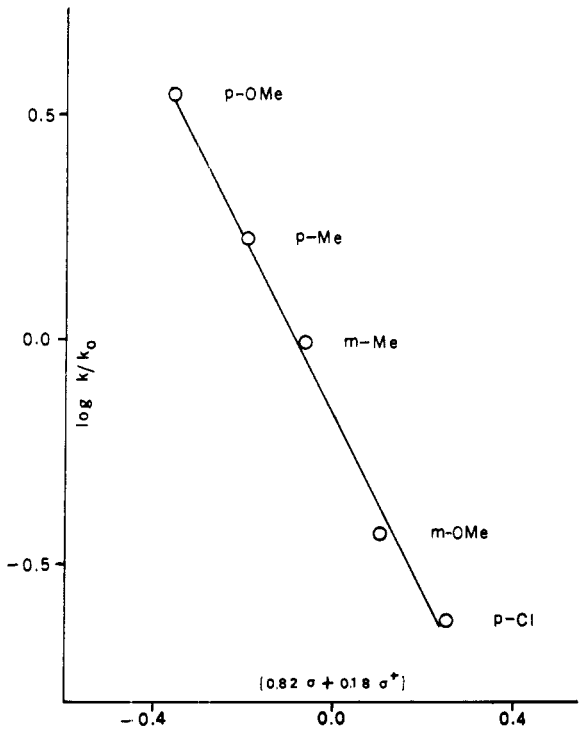


Figure 4. Yukawa–Tsuno plot for the acetolysis of π-tricarbonylchromium-complexed neophyl methanesulfonates at 99.5 °C: $\log (k/k_0) = -1.97[\sigma + 0.18(\sigma^+ - \sigma)] - 0.162$.

The Yukawa–Tsuno correlations appear to be compatible with our earlier suggestion that π-tricarbonylchromium acts as an electron sink to attenuate the effect of substituents on the ring. The fact that $\rho = -1.97$ and $r = 0.18$ for the complexes but that $\rho = -3.39$ and $r = 0.43$ for the noncomplexed derivatives implies that the substituent itself is less conjugated with the developing positive charge during the solvolysis of the complexes. The extent of back-bonding by the carbonyl groups of a π-(arene)chromium tricarbonyl complex is known to depend upon the electronic effect of substituents on the ring.[12] This electronic interaction between substituent and metal apparently decreases the ability of a substituent to conjugate with the developing cationic center during the solvolysis of a chromium tricarbonyl complex.

Complexes substituted with activating groups (p-CH_3O, p-CH_3, m-CH_3) are solvolytically less reactive than their noncomplexed counterparts while those substituted with deactivating groups (m-CH_3O, p-Cl) are more reactive: all are well correlated by the same Yukawa–Tsuno relation (Figure 4). These facts suggest that π-tricarbonylchromium is electronically amphoteric, i.e., capable of conjugative electron withdrawal or donation as required. When a p-nitro group is used to model inductive electron withdrawal,[2] π-tricarbonylchromium appears to accelerate the acetolysis rates of **5a**- and **6a**-OMs by factors of 700 and 1000 times, respectively, at 100 °C.

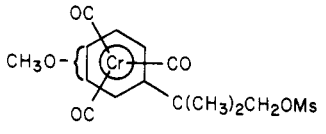
The unusual "amphoteric" effect may also explain the fact that complexed tricarbonylchromium, unlike p-nitro, does not inhibit aryl migration during solvolysis. Whereas ~28% of the acetolysis products of 7-OMs at 137 °C do not involve aryl migration,[8] all of the acetolysis products from **6a**-OMs at ~100 °C result from π-complexed aryl migration. Apparently π-tricarbonylchromium can still stabilize phenonium-ion-like transition states or intermediates (Scheme I) by conjugative electron donation in spite of its large inductive electron withdrawal.

(12) (a) R. D. Fischer, *Chem. Ber.*, **93**, 195 (1960); (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, pp 684–7.

Table II. Yields, Physical Properties, and Analyses of Methanesulfonates

	5-OMs	5a-OMs	6-OMs	6a-OMs
% yield from ROH	67		77	
% yield from ROMs		33		56
mp, °C	oil at 25 °C	87–88	40–41	79–80
% C calcd	55.79	45.68	50.28	42.16
found	55.90	45.80	50.04	42.29
% H calcd	7.02	4.60	5.75	3.79
found	7.10	4.64	5.56	3.88
% Cl calcd				8.89
found				8.79
% O calcd	24.77	28.40	18.27	24.07
found	24.56	28.19	18.09	24.18
% S calcd	12.41	8.13		
found	12.59	7.96		

It seems likely from this study that the rate enhancements which apparently accompany the π-complexation of neophyl derivatives do not involve direct d-orbital bridging by chromium (path a, Scheme I) in the rate-limiting step. If these d^8 complexes adopt the expected staggered configuration for the tricarbonyl group relative to the ring carbons[13] (structure I), electronic interactions



I

between chromium and methoxyl and between chromium and a developing β-cationic center are expected to be comparable in both the meta and para derivatives. Thus, were d-orbital bridging to be important, the solvolytic rate of **2a**-OMs should be comparable to and not an order of magnitude greater than that of **6a**-OMs. Apparently solvolytic rate enhancements by π-tricarbonylchromium are due to σ–π *homo*conjugation (Scheme I, path b) and/or to a charge–dipole effect similar to that suggested earlier[4a] or to some as yet unrecognized mode of interaction.

Experimental Section[14]

Preparation of the Noncomplexed Methanesulfonates. The methanesulfonates were prepared as reported previously[2] from the known 2-(p-chlorophenyl)-[15] and 2-(m-methoxyphenyl)-2-methylpropanols.[16] Melting points, analyses, and yields are recorded in Table II.

2-(p-Chlorophenyl)-2-methylpropyl methanesulfonate (6-OMs): IR (CCl_4) 3030, 1490 (aromatic), 2940, 2850 (CH), 1390, 1160 (OSO_2), 1380 cm^{-1} (>$C(CH_3)_2$); NMR ($CDCl_3$) 7.22 (4 H, s, aromatic), 4.12 (2 H, s, >CCH_2O), 2.77 (3 H, s, OSO_2CH_3), 1.37 (>$C(CH_3)_2$).

2-m-Anisyl-2-methylpropyl methanesulfonate (5-OMs): IR (CCl_4) 3030, 1590 (aromatic), 2810, 1240 (aromatic methoxy), 1420, 1160 (OSO_2), 1380 cm^{-1} (>$C(CH_3)_2$); NMR ($CDCl_3$) δ 7.5–6.5

(13) I. F. Taylor, Jr., E. A. H. Griffith, and E. L. Amma, *Acta Crystallogr., Sect. B*, **32**, 653 (1976), and references cited therein.

(14) Melting points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, West Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrophotometer, Model 337, and a Varian A-60 or a Perkin-Elmer R-32 NMR spectrometer using tetramethylsilane as an internal standard. Vapor-phase gas chromatographic analyses utilized a Varian Model 1800 chromatograph equipped with a 12 ft × $^1/_4$ in. aluminum column packed with 15% Carbowax 20-M on 60–80 mesh Chromosorb W. Helium was used as a carrier gas with flow rates of 100–120 mL/min.

(15) M. G. Jones and J. L. Coke, *J. Am. Chem. Soc.*, 91, 4284 (1969).

(16) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, 78, 4801 (1956).

(4 H, m, aromatic), 4.29 (2 H, s, $>CCH_2O$), 3.90 (3 H, s, H_3CO), 2.90 (3 H, s, OSO_2CH_3), 1.52 (6 H, s, $>C(CH_3)_2$).

Preparation of the π-Complexed Methanesulfonates. The π-complexed methanesulfonates were prepared by treatment of the noncomplexed methanesulfonates with chromium hexacarbonyl in a Strohmeier apparatus as described previously.[3] Melting points, analyses, and yields are recorded in Table II.

2-[π-(p-Chlorophenyl)chromium tricarbonyl]-2-methylpropyl methanesulfonate (6a-OMs): IR ($CHCl_3$) 3030, 1450 (aromatic), 1970, 1900 (C≡O), 1400, 1160 (OSO_2), 1380 cm^{-1} ($>C(CH_3)_2$); NMR ($CDCl_3$) δ 5.65–5.26 (4 H, complex m, aromatic), 4.00 (2 H, s, $>CCH_2O$), 2.93 (3 H, s, OSO_2CH_3), 1.29 (6 H, s, $>C(CH_3)_2$).

2-[π-(m-Anisyl)chromium tricarbonyl]-2-methylpropyl methanesulfonate (5a-OMs): IR ($CHCl_3$) 3030, 1530 (aromatic), 2800, 1250 (aromatic methoxyl), 1970, 1900 (C≡O), 1400, 1150 (OSO_2), 1380 cm^{-1} ($>C(CH_3)_2$); NMR [$(CD_3)_2CO$] δ 5.90–5.17 (4 H, complex m, aromatic), 4.17 (2 H, s, $>CCH_2O$), 3.33 (3 H, s, OCH_3), 3.01 (3 H, s, OSO_2CH_3), 1.44 (6 H, s, $>C(CH_3)_2$).

Products from the Acetolysis of 2-[π-(p-Chlorophenyl)-chromium tricarbonyl]-2-methylpropyl Methanesulfonate (6a-OMs). A 25-mL sample of 0.033 M **6a**-OMs and 0.05 M sodium acetate in oxygen-free, anhydrous acetic acid was heated under nitrogen at 100 °C for 20 h (11 half-lives), cooled, poured over ice, and extracted with three 20-mL portions of pentane. The combined extracts were washed with excess, cold, saturated aqueous sodium carbonate solution and with two portions of cold water and dried over anhydrous magnesium sulfate. When spotted on a thin-layer plate coated with silica gel and developed with 50/50 ether/pentane, three yellow spots were evident.

The yellow solution was decomplexed by using 1.5 g (2.7 mmol) of ceric ammonium nitrate in 30 mL of acetone and 20 mL of water.[2] The mixture was stirred until the yellow color had disappeared (1 h), and the ether–pentane layer was washed with water, filtered through anhydrous sodium sulfate, and concentrated to ~10 mL. A GLC analysis on a 12-ft Carbowax column showed three components having relative retention times (relative peak areas in parentheses) of 4.7 (34%), 6.1 (12%), and 21.8 (54%). The first and second components were identified as 3-(p-chlorophenyl)-2-methyl-1-propene (**8**) and 1-(p-chlorophenyl)-2-methyl-1-propene (**9**), respectively, by comparison of their IR and NMR spectra with those of authentic samples. The third component was identified as 3-(p-chlorophenyl)-2-methyl-2-propyl acetate (**10**) from the following spectral characteristics: IR (CCl_4) 3030, 1500 (aromatic), 2950, 2900 (CH), 1730 (C=O), 1380, 1360 ($>C(CH_3)_2$), 1235, 1020 cm^{-1} (C—O, acetate); NMR ($CDCl_3$) δ 7.29–7.1 (4 H, A_2B_2 q, aromatic), 3.0 (2 H, s, $O>CCH_2$–aryl), 1.9 (3 H, s, $OCOCH_3$), 1.4 (6 H, s, $>C(CH_3)_2$).

Kinetic Studies. The acetolysis rates were measured titrimetrically, with the ampule technique described previously,[1] on ~0.03 M solutions of the methanesulfonate in acetic acid buffered with 0.05–0.1 M sodium acetate and containing ~1% acetic anhydride. Oxygen-free solutions prepared as described previously[1] were employed with the complexes.

Registry No. 1-OMs, 29240-45-7; **1a**-OMs, 31973-95-2; **2**-OMs, 29240-46-8; **2a**-OMs, 72938-23-9; **3**-OMs, 29240-47-9; **3a**-OMs, 31833-07-5; **4**-OMs, 29240-48-0; **4a**-OMs, 31833-08-6; **5**-OMs, 72925-77-0; **5a**-OMs, 72938-23-9; **6**-OMs, 72925-78-1; **6a**-OMs, 72926-38-6; **7**-OMs, 72925-79-2; **8**, 23063-65-2; **9**, 19366-15-5; **10**, 72925-80-5.

Transmission of Substituent Effects in Thiophenes. Infrared and Carbon-13 Nuclear Magnetic Resonance Studies

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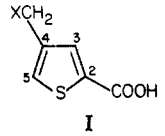
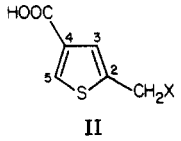
The carbon-13 NMR spectra in Me_2SO-d_6 and the infrared carbonyl stretching frequencies were determined for nine 4-(substituted methyl)-2-thiophene-2-carboxylic acids (I) and for nine 2-(substituted methyl)-4-thiophene carboxylic acids (II). Chemical shift assignments were made by employing chemical shift and intensity arguments and by interpretation of the proton-coupled spectra. The assignments in series I were supported by a lanthanide shift reagent study on Ia. Infrared carbonyl stretching frequencies were determined in chloroform and tetrachloromethane solutions. The infrared stretching frequency data were correlated reasonably well with σ_I constants, whereas the NMR data gave much poorer correlations with single-parameter approaches. The conclusions drawn from both the IR and NMR data are consistent with previously reported pK_a and carbon-13 NMR data which indicated unequal transmission of substituent effects in the two series. All of the data, pK_a, IR, and NMR, for transmission of substituent effects can be explained in terms of differences in the relative coplanarity of the two systems and its consequences on the π-inductive effect.

Reports have recently appeared describing the effect of substituents on the acidity and the carbon-13 chemical shifts in $CDCl_3$ of 4-methyl-2-thiophenecarboxylic acids (I) and 2-methyl-4-thiophenecarboxylic acids (II) substituted on the methyl group.[1] The pK_a values for both series were reasonably well correlated with σ_I values. Interestingly, the ρ value for series I was approximately 1.5 times larger than that for series II. Limited correlations were observed between the carbon-13 data and substituent constants. These results indicate that transmission of substituent effects is dramatically changed by reversing the location of the reaction site and the substituent in this



I



II

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