observed that optically active phosphine oxide was reduced by trichlorosilane to give phosphine with retention of configuration. Based on this stereochemical observation, which is yet to be complemented by kinetics observation, the following mechanism was proposed.

Our kinetics results would then lend credence to this proposal. It should be pointed out that if an intermediate involving a phosphorane structure is proposed for this reaction, according to the stereochemical analysis of displacement reactions at phosphorus by Mislow, *et al.*,[26] a cyclic constraint has to be introduced to account for the retention of configuration.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the National Research Council of Canada in the form of a studentship to A. M. is also gratefully acknowledged.

(26) K. E. Debruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969). See also P. D. Hensen, K. Naumann, and K. Mislow, *ibid.*, **91**, 5645 (1969).

π-Complexed β-Arylalkyl Derivatives. II. The Preparation and Acetolysis of 2-[π-(Aryl)chromium tricarbonyl]-2-methyl-1-propyl Methanesulfonates[1a]

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Abstract: The π-(arene)chromium tricarbonyl complexes of 2-phenyl-2-methyl-1-propyl (neophyl) and *p*-methoxy-, *p*-methyl-, and *m*-methylneophyl methanesulfonates have been prepared and their acetolysis rates and products determined. At 75° the complexed derivatives are 1.8, 0.091, 0.45, and 0.91 times, respectively, as reactive as their noncomplexed counterparts. Each yields the π-aryl-migrated acetate, 3-[π-(aryl)chromium tricarbonyl]-2-methyl-2-propyl acetate, as the major product together with a mixture of π-complexed olefins. The acetolysis rates of the complexes at 75° are correlated by the relation log k (complex) $= -0.78\sigma^+ - 4.40$; those of the noncomplexed series by log $k = -2.35\sigma^+ - 4.56$. The meaning of these correlations is discussed and their difference is ascribed to a strong inductive electron withdrawal by the tricarbonylchromium combined with a conjugative effect which tends to suppress 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 it is estimated that the acetolysis rates of the complexed *p*-hydrogen-, *p*-methoxy-, *p*-methyl-, and *m*-methylneophyl methanesulfonates are enhanced by factors of 1600, 80, 400, and 800 times, respectively, at 75°. Steric buttressing, σ-π-type delocalization, and direct d-orbital bridging are considered as possible sources of the observed effect of π-complexation on the rates and course of these acetolyses.

In the previous paper of this series[2] we reported the acetolytic rates and products of chromium tricarbonyl-complexed D-, L-, DL-*threo*-, DL-*erythro*-3-phenyl-2-butyl, and DL-*erythro*-2-phenyl-3-pentyl methanesulfonates and compared them with those of the noncomplexed compounds. Among other effects we noted that prior π-complexation decreases the overall acetolysis rate slightly and inhibits aryl migration completely. After making a correction for the apparent inductive effect of the chromium tricarbonyl group we concluded that the acetolysis rates of the complexed *threo*- and *erythro*-3-phenyl-2-butyl methanesulfonates may be enhanced by factors of 33 and 6.8 times, respectively. Steric buttressing and inhibition of phenyl migration, σ-π-type delocalization, and direct d-orbital bridging were considered as possible sources of these effects but we were unable to make a clear distinction among them because so little was known about the electronic effect of the chromium tricarbonyl group itself. In order to examine this aspect of the problem in greater detail and to ascertain whether a π-complexed aryl group would migrate under more favorable circumstances, we have prepared and examined the acetolytic reactivities of a series of chromium tricarbonyl-complexed 2-phenyl-2-methyl-1-propyl- (neophyl-) type methanesulfonates.

Methods and Results

Each of the required methanesulfonates, **1**- to **4**-OMs, was prepared from the known 2-aryl-2-methyl-1-propanol[3] in the usual manner[2] and converted to the yellow, crystalline, apparently air stable, chromium tricarbonyl complex as described previously,[2] *cf.* Chart I.

Acetolyses of these primary methanesulfonates were conducted and the products were determined in the manner described earlier.[2] Control experiments were again employed to demonstrate that the decomplexation and reduction procedure used in the analysis of the complexed derivatives did not isomerize the organic

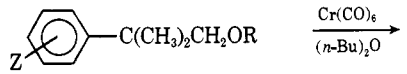
(1) (a) Portions of this work were presented at the 38th Annual Meeting of the South Carolina Academy of Science, Columbia, S. C., April 1965 [*Bull. S. Carolina Acad. Sci.*, **XXVII**, 52 (1965)] and at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstract 008S; (b) NSF Trainee 1968–1970.

(2) R. S. Bly and R. L. Veazey, *J. Amer. Chem. Soc.*, **91**, 4221 (1969).

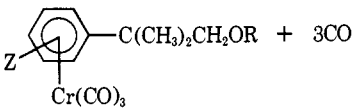
(3) (a) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *ibid.*, **65**, 1469 (1943); (b) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (c) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

portion of the ligand. The products of the acetolyses are summarized in Charts II and III. In the case of

Chart I

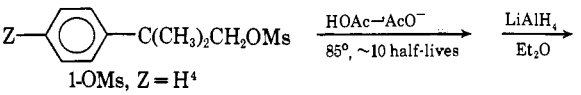


1-OMs, R = Ms; Z = H
2-OMs, R = Ms; Z = *p*-CH_3O
3-OMs, R = Ms; Z = *p*-CH_3
4-OMs, R = Ms; Z = *m*-CH_3
5-OBs, R = Bs; Z = *p*-NO_2

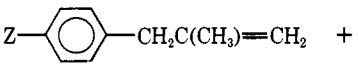


1a-OMs, R = Ms; Z = H
2a-OMs, R = Ms; Z = *p*-CH_3O
3a-OMs, R = Ms; Z = *p*-CH_3
4a-OMs, R = Ms; Z = *m*-CH_3

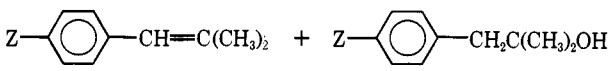
Chart II



1-OMs, Z = H[4]
2-OMs, Z = OCH_3
3-OMs, Z = CH_3



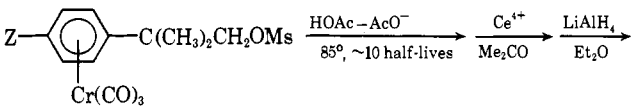
6, Z = H (45%)
7, Z = OCH_3 (44%)
8, Z = CH_3 (43%)



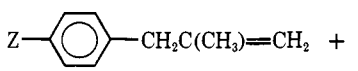
9, Z = H (29%)
10, Z = OCH_3 (31%)
11, Z = CH_3 (34%)

12-OH, Z = H (26%)
13-OH, Z = OCH_3 (25%)
14-OH, Z = CH_3 (23%)

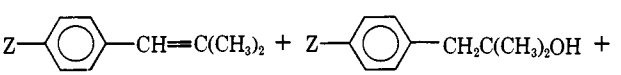
Chart III



1a-OMs; Z = H[6]
2a-OMs; Z = OCH_3
3a-OMs; Z = CH_3

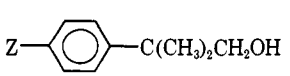


6, Z = H (32%)
7, Z = OCH_3 (51%)
8, Z = CH_3 (22%)



9, Z = H (10%)
10, Z = OCH_3 (0%)
11, Z = CH_3 (9%)

12-OH, Z = H (58%)
13-OH, Z = OCH_3 (49%)
14-OH, Z = CH_3 (69%)



1-OH, Z = H (trace)[7]
2-OH, Z = OCH_3
3-OH, Z = CH_3 (trace)[7]

(4) Heck and Winstein[3o] report 32.5% **6**, 33.8% **9**, 33.4% **12**-OAc and 0.3% **1**-OH from the acetolysis of **1**-OBs at 75° for 28 hr (10 half-lives) while Saunders and Paine[5] report 16% **6**, 78.1% **9**, 5% **12**-OAc, 0.29% 2-phenyl-*cis*-2-butene, and 0.6% 1-phenyl-2-methyl-1-propyl acetate from the acetolysis of **1**-OTs at ~119° for 24 hr (120 half-lives).

(5) W. H. Saunders, Jr., and R. H. Paine, *J. Amer. Chem. Soc.*, **83**, 882 (1961).

(6) Formolysis of **1a**-OMs in buffered solution at 70° for 0.5 hr (greater than 10 but less than 30 half-lives) followed by decomplexation and reduction yields a mixture consisting of 4.8% **6**, 3.1% **9**,, and 92.1% **12**-OH, *cf.* Experimental Section. Saunders and Paine[5] report that the formolysis of **1**-OTs at ~100° for 22 hr (>6000 half-lives) yields 5.2% **6**, 59.4% **9**, 29.4% **12**-OCOH, 0.69% 2-phenyl-*cis*-2-butene and 5.3% 1-phenyl-2-methyl-1-propyl formate.

(7) Identification is tentative, see Experimental Section.

(8) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956).

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

(10) In 50% ethanol at 25° the pK_a of phenylacetic acid is 5.64 while that of the *p*-nitro and π-chromium tricarbonyl derivatives is 5.01 and 5.02, respectively.[11]

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

1a-OMs, the π-complexed products were actually isolated and characterized, *cf.* Experimental Section.

Unlike their 2-phenyl-3-pentyl and 3-phenyl-2-butyl counterparts,[2] both the complexed and the noncomplexed 2-aryl-2-methyl-1-propyl derivatives produce aryl-migrated products exclusively. Here too the complexes yield considerably less total olefin, but a larger proportion is the 3-aryl-2-methyl-1-propene or nonconjugated type.

Titrimetric acetolysis constants for the complexed and noncomplexed methanesulfonates were determined as detailed in the Experimental Section and elsewhere[2] under conditions identical with those used in the product studies. The kinetic data are summarized and compared with those of some related compounds[3c,8,9] in Table I.

As in the 3-phenyl-2-butyl cases examined earlier,[2] prior chromium tricarbonyl complexation decreases both the enthalpy and the entropy of activation for the acetolyses of the 2-aryl-2-methyl-1-propyl (neophyl-type) methanesulfonates. With the exception of 2-[π-(phenyl)chromium tricarbonyl]-2-methyl-1-propyl methanesulfonate (**1a**-OMs) whose reactivity exceeds that of the noncomplexed derivative, **1**-OMs, by 1.8 times at 75°, π-complexation also decreases the overall acetolysis rates of these β-arylalkyl methanesulfonates. The *p*-methoxy, *p*-methyl, and *m*-methyl complexes are, respectively, 0.091, 0.45, and 0.91 times as reactive at 75° as their noncomplexed counterparts.

The effect of added salts on the acetolysis rate has been tested in the case of **1**-OMs and its π-complex, **1a**-OMs, *cf.* Table II.

In contrast to the 3-phenyl-2-butyl cases,[2] π-complexation appears to *decrease* slightly the sensitivity of the acetolysis rate of neophyl methanesulfonate to added acetate ion, *cf.* the acetate *b* values of **1**- and **1a**-OMs.

Discussion

The chromium tricarbonyl group appears to participate in the acetolysis of a 2-[π-(aryl)chromium tricarbonyl]-2-methyl-1-propyl methanesulfonate. The experimentally identical ionization constants of *p*-nitro- and chromium tricarbonyl-complexed phenylacetic acids[10] led Nicholls and Whiting to suggest that "the π-bound tricarbonylchromium group withdraws electrons at least as strongly as a *p*-nitro group."[11] Since the ionization of arylacetic acids does not involve direct conjugation between the aryl and the carboxyl groups and is not overly sensitive to the bulk or position

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

Run	Compd	Temp,[a] °C	10^6k, sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu
1, 2	**1**-OMs[b]	69.5	12.1 ± 0.05	25.8[c]	−5.96[c]
3, 4		87.4	83.55 ± 0.95		
5			85.6[d]		
6			81.8[e]		
7			146[f]		
8			80.9[g]		
9			191[h]		
10, 11		101.1	323.5 ± 4.5		
		75.0	23.3[i]		
	1-OTs		20.0 ± 0.2[i]	26.0[k]	−5.7[k]
	1-OBs		68.4 ± 0.3[i]	25.5[k]	−4.6[k]
12, 13	**1a**-OMs[b]	69.5	23.45 ± 0.95	24.2[l]	−9.28[l]
14, 15		87.4	132 ± 2		
16			133[m]		
17			133[d]		
18			120[e]		
19			228[f]		
20			137[g]		
21, 22		101.1	521.5 ± 4.5		
		75.0	40.6[i]		
23, 24	**2**-OMs[n]	24.9	6.04 ± 0.02	22.6[o]	−6.55[o]
25, 26		39.8	41.4 ± 0.05		
27		55.4	254[e]		
28, 29		55.5	231.5 ± 1.5		
		75.0	1740[p]		
	2-OTs[j]		1690	23.2	−4.4
30	**2a**-OMs[q]	57.2	24.8	23.1	−10.0
31		69.3	92.2		
32		87.3	508		
		75.0	159[i]		
33, 34	**3**-OMs[r]	55.5	19.2 ± 0.2	24.2[s]	−6.72[s]
35, 36		70.3	103.5 ± 0.5		
37, 38		85.0	440.5 ± 0.5		
39			423[e]		
		75.0	164[i]		
	3-OBs[k]		497 ± 5	24.7	−3.1
40, 41	**3a**-OMs[r]	70.3	45.75 ± 0.25	23.4[t]	−10.5[t]
42, 43		85.0	198 ± 5		
44			178[e]		
45, 46		97.4	607 ± 5		
		75.0	74.2[i]		
47, 48	**4**-OMs[n]	54.8	4.73 ± 0.06	25.1	−6.44
49, 50		69.3	25.15 ± 0.45		
51, 52		87.6	172.5 ± 0.5		
		75.0	47.0[i]		
	4-OBs[k]		131.8 ± 0.5	25.8	−2.4
53, 54	**4a**-OMs[n]	54.9	4.945 ± 0.125	23.6	−11.1
55, 56		69.3	24.35 ± 0.05		
57, 58		86.7	134 ± 1		
		75.0	43.0[i]		
	5a-OBs[u]		0.0760	29.1	−7.9

[a] Controlled to ±0.03°. [b] Contains 0.0393–0.0410 *M* ROMs and 0.0995 *M* sodium acetate unless otherwise specified. [c] Computed from runs 1–4, 10 and 11. [d] Contains 0.1978 *M* sodium acetate. [e] Contains no sodium acetate. [f] Contains 0.0992 *M* lithium perchlorate. [g] Contains 0.100 *M* sodium methanesulfonate. [h] Contains 0.0989 *M* lithium perchlorate but no sodium acetate. [i] Interpolated from data at other temperatures. [j] Reference 8. [k] Reference 3c. [l] Computed from runs 12–15, 21, and 22. [m] Contains 0.0197 *M* ROMs. [n] Contains 0.0196–0.0209 *M* ROMs and 0.0495–0.0497 *M* sodium acetate unless otherwise specified. [o] Computed from runs 23–26, 28, and 29. [p] Extrapolated from data at other temperatures. [q] Contains 0.0129–0.0133 *M* ROMs and 0.0496 *M* sodium acetate. [r] Contains 0.0193–0.0209 *M* ROMs and 0.0461 *M* sodium acetate unless otherwise specified. [s] Computed from runs 33–38. [t] Computed from runs 40–43, 45, and 46. [u] Reference 9.

Table II. Dependence of Apparent First-Order Acetolysis Constants of 2-Aryl-2-methyl-1-propyl-type Sulfonates upon Added Salts

Compd	Temp, °C	$10^6k_t^0$, sec^{-1}	—Value of "*b*" for added— NaOAc	NaOMs	$LiClO_4$
1-OTs[a]	75	20.0		3.2[b]	12.5
1-OBs[a]	75	68.4	1.1[c]	2.9[b]	10.0
1-OMs	87.4	81.6[d]	0.25	−0.33[e]	7.7[e]
1a-OMs	87.4	131[d,f]	0.078	0.38[e]	7.4[e]

[a] Reference 8. [b] Value for added lithium *p*-toluenesulfonate. [c] Value for added lithium acetate. [d] Calculated assuming $k_t = k_t^0(1 + b[NaOAc])$.[8] [e] Assuming $k_t = k_t^0(1 + b_1[NaOAc] + b_2[salt\ 2])$.[2,8] [f] Note: (k_t^0) extrapolated = 1.1(k_t^0) measured, *cf.* Table I, run 18.

of the aryl substituent,[12] it is likely that the effect of both the chromium tricarbonyl and *p*-nitro groups is largely inductive in this instance.[14,15] Hence the ratio of the acetolytic rate constants of 2-*p*-nitrophenyl- and 2-phenyl-2-methyl-1-propyl *p*-bromobenzenesulfonates—0.0011 times at 75°, *cf.* Table I[9]—may be taken as a measure of the extent to which the acetolysis of a 2-[π-(aryl)chromium tricarbonyl]-2-methyl-1-propyl derivative is inductively retarded at this temperature by the chromium tricarbonyl moiety. Dividing the observed reactivity ratios of the complexed and noncomplexed methanesulfonates at 75°, *cf.* Results Section, by this expected inductive retardation yields estimates of the approximate rate enhancement attributable to the chromium tricarbonyl group in each case—about 1600 times in the unsubstituted 2-phenyl-2-methyl-1-propyl complex (**1a**-OMs) and 80, 400, and 800 times, respectively, in the *p*-methoxy, *p*-methyl, and *m*-methyl derivatives, **2a**-, **3a**-, and **4a**-OMs. These values are considerably larger than the factors of 33 and 6.8, estimated in a similar manner for the acetolyses of DL-*threo*- and *erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonates at 85°.[2]

Although the steric bulk of a π-complexed tricarbonylchromium has been likened qualitatively to that of "a large *ortho* substituent,"[17] quantitative

(12) For example, the pK_a's of *o*-, *m*-, and *p*-nitrophenylacetic acids in water at 25° are 4.01, 3.97, and 3.85, respectively.[13]

(13) G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth & Co., Ltd. London, 1961, p 412, and references cited therein.

(14) A referee has suggested that a comparison of the acidities of *p*-nitro- and π-chromiumtricarbonyl-substituted phenylacetic acids might not provide a realistic estimate of the inductive effect of the tricarbonylchromium group since the acidity of the complexed acid may be lowered by intramolecular hydrogen bonding to either the chromium or one of the carbonyls. We have been unable to detect such an effect experimentally, *cf.* Experimental Section, but cannot completely rule out this possibility. If important, it would cause us to *underestimate* both the electron withdrawing ability of the complex and the extent of its participation during solvolysis.

(15) Their near equivalence has also been noted in the alkaline hydrolysis of π-tricarbonylchromium- and *p*-nitro-substituted methyl benzoates;[16] another case where direct electron withdrawal by resonance is relatively unimportant.

(16) G. Klopman and F. Calderazzo, *Inorg. Chem.*, **6**, 977 (1967).

(17) Nicholls and Whiting, after noting the *decreased acidity* in 50% ethanol of the π-complexed benzoic acid (pK_a = 4.77) relative to *p*-nitrobenzoic (pK_a = 4.48), suggested that this difference results from steric hindrance to solvation by the tricarbonylchromium and likened the group in this respect to "a large *ortho* substituent."[11] We assume that this analogy is based upon the essentially identical pK_a's (3.44–3.46) of *o*-*t*-butyl, *m*-, and *p*-nitrobenzoic acids in water at 25°,[18] but doubt the validity of such a comparison. Relatively nonpolar *ortho* substituents normally *increase* the acidity of a benzoic acid—the pK_a's in water at 25° of *m*- and *p*-*t*-butylbenzoic acids are reported to be 4.28 and 4.40, respectively—presumably by preventing the carboxyl group and the aromatic ring from becoming coplanar.[18] If anything, the steric bulk of a π-complexed group should *enhance* the coplanarity of an sp^2 center adjacent to and conjugated with an aromatic ring.

(18) H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," Vol. 1, E. A. Braude

comparisons with σ-bonded aryl substituents are rendered difficult by the relatively unique geometry of the complex. The largest steric effect of π-bound chromium tricarbonyl is probably to be expected in a reaction whose rate limiting step entails extensive hybridizational change at an atom in or adjacent to the aromatic ring itself. Yet such an effect, if present, is certainly not dominant for both nucleophilic aromatic substitution of aryl halides[11,19] and the saponifications of substituted methyl benzoates[16] are more facile in the π-chromium tricarbonyl derivatives than in their noncomplexed counterparts. Since the steric effect of a π-bound metal moiety should generally be even less important when the reactive site in the ligand is more remote, we infer that the enhancements calculated for the solvolyses of π-complexed β-arylalkyl derivatives, especially the larger values encountered in the neophyl-type derivatives reported here, are due predominantly to electron donation by the tricarbonylchromium.

There are ample theoretical[20] and experimental[21] reasons for suspecting that a π-complexed chromium tricarbonyl group is capable of strong electron withdrawal by resonance under appropriate circumstances, but the extent of its ability to *donate* electrons in this manner is less certain. Though π-arenechromium tricarbonyls are generally reported to be less susceptible to electrophilic aromatic substitution than their noncomplexed analogs,[11,24,25] they appear in occasional instances to be more reactive under such conditions.[19,26] Unless steric effects in these systems are much larger than they now appear to be, *vide supra*, the decreased acidity of π-(benzoic acid)chromium tricarbonyl relative to *p*-nitrobenzoic acid[11,22] and the lower stretching frequency of the ester carbonyl of methyl π-(benzoate)-chromium tricarbonyl (1732 cm^{-1})[27] relative to that of methyl *p*-nitrobenzoate (1735 cm^{-1})[28] may also reflect some back donation by the π-bound tricarbonylchromium. The hydrolyses of chromium tricarbonyl-complexed benzyl and benzhydryl chlorides probably are sterically accelerated, but both the greatly enhanced rates which have been reported in these cases[29] as well as the increased pK_{R^+} of π-(benzyl alcohol)chromium tricarbonyl relative to that of benzyl alcohol itself[30] certainly imply extensive electron donation from the metal to the ligand.

Aside from the calculated rate enhancements, the most convincing evidence of electron donation by the metal tricarbonyl that can be cited from our results is probably that of the product studies. The work of Thompson and Cram[31] and of Tanida, Tsuji, Ishitobi, and Irie[9] in the 3-aryl-2-butyl and 2-aryl-2-methyl-1-propyl (neophyl-type) systems, respectively, clearly indicates that electron withdrawal by a *p*-nitro group inhibits aryl participation and migration during acetolysis. In the latter case 28% of the products *do not* result from aryl migration. Even though its inductive electron withdrawal is comparable and its ability to withdraw electrons by resonance may be greater than that of *p*-nitro,[21] π-complexed chromium tricarbonyl does not inhibit aryl migration to the point where either methyl migration or direct displacement is apparent in the acetolysis of 2-[π-(aryl)chromium tricarbonyl]-2-methyl-1-propyl methanesulfonates.[32]

In addition to its electron-withdrawing inductive effect and its electron-donating resonance or "back-bonding" effect π-tricarbonylchromium appears to attenuate or "buffer" the resonance effect of other aryl substituents. Both the complexed and noncomplexed 2-aryl-2-methyl-1-propyl methanesulfonates give reasonably linear, modified Hammett correlations of log k_t (for acetolysis at 75°) *vs.* σ^+,[34] *cf.* Figure 1; however, the slopes of these plots are quite different: $\rho = -2.35$ for the noncomplexed derivatives,[35,36] -0.78 for the complexes. Similar effects have been detected by Klopman and Calderazzo in the saponification of chromium tricarbonyl-complexed and noncomplexed methyl benzoates in 56% acetone at 25°[16] and by Fritz and Kreiter[37] in the nmr spectra of some substituted π-(arene)metal carbonyls.

It is not presently known whether these differences in slope should actually be attributed to changes in the reaction constant (ρ),[16] the substituent constants (σ^+), or both. Since the steric and/or inductive effect of a π-bound tricarbonyl chromium is expected to remain approximately constant throughout a single reaction series and to be independent of, rather than proportional to, the electronic nature of a σ-bonded aryl substituent, changes in the magnitudes of these effects should alter the intercept rather than the slope of a modified Hammett plot. For this reason we prefer to consider that,

and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 603 ff, and references cited therein.

(19) D. A. Brown and J. R. Raju, *J. Chem. Soc., A*, 40 (1966).

(20) D. A. Brown, *ibid.*, 4389 (1962).

(21) The pK_a of π-(phenol)chromium tricarbonyl in water at 22° is reported to be 6.51.[22] If steric effects are assumed to be negligible—they do not appear to be large in *ortho*-substituted phenols unless steric inhibition of resonance is a factor[18]—this corresponds to a σ^- value for π-Cr(CO)$_3$ of about 1.6. The σ^- value of *p*-nitro is 1.27.[23]

(22) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958).

(23) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 211.

(24) G. E. Herberich and E. O. Fischer, *Chem. Ber.*, **95**, 2803 (1962).

(25) For reviews, see (a) K. Plesske, *Angew. Chem.*, **74**, 301 (1962); (b) H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid-Metal Complexes," The Ronald Press Co., New York, N. Y., 1966, p 59 ff; (c) J. P. Collman in "Transition Metal Chemistry," Vol. 2, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, p 1; (d) M. L. H. Green in "Organo-Metallic Compounds," Vol. 2, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen & Co., Ltd., London, 1968, p 180 ff.

(26) (a) V. N. Setkina, N. K. Baranetskaya, K. N. Anisimov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1873 (1964).

(27) G. Klopman and K. Noack, *Inorg. Chem.*, **7**, 579 (1968).

(28) We thank Dr. James R. Durig and Mr. Charles Pate for this determination.

(29) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, 4, 324 (1965).

(30) W. S. Trahanovsky and D. K. Wells, *J. Amer. Chem. Soc.*, **91**, 5870, 5871 (1969).

(31) (a) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967); (b) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969).

(32) The partial rate factors for methyl and aryl migration during the acetolysis of **1**- and **1a**-OMs at 85° (the temperature of the product studies) are $p_{CH_3} \leq 1.6 \times 10^{-7}$ sec^{-1}, $p_{phenyl} \approx 6.5 \times 10^{-5}$ sec^{-1} and $p_{CH_3} \leq 2.7 \times 10^{-7}$ sec^{-1}, $p_{aryl} \approx 1.1 \times 10^{-4}$ sec^{-1}, respectively. Assuming an OBs/OMs rate ratio of 20.0/6.50 ≃ 3.1, *cf.* Table I, we estimate from Tanida's data[9] that p_{CH_3} would be $\simeq 1 \times 10^{-8}$ sec^{-1} and $p_{aryl} \simeq 6 \times 10^{-8}$ sec^{-1} for the acetolysis of **5**-OMs at this temperature.[33] Thus the migratory aptitude of π-(phenyl)chromium tricarbonyl exceeds that of *p*-nitrophenyl by about 1800 times.

(33) Based upon product studies at 137°, *cf.* ref 9, footnote 11.

(34) Note that it is *not* possible to fit the data for both the complexed and the noncomplexed derivatives to a single line defined by the equation: $\log (k_t/k_t^0) = \rho\Sigma\sigma^+$, where $\Sigma\sigma^+$ incorporates a single, invarient value for the substituent contant of π-Cr(CO)$_3$.

(35) For the acetolysis of *meta*- and *para*-substituted tosylates at 75°,[8c,9] $\rho = -2.96$.

(36) The existence of separate linear free energy relations for the complexed and noncomplexed methanesulfonates means that the acetolysis rates of like-substituted complexed and noncomplexed derivatives are also linearly related: $\log (k_t)_{complex} = 0.331 \log (k_t)_{noncomplex} - 2.888$.

(37) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **7**, 427 (1967).

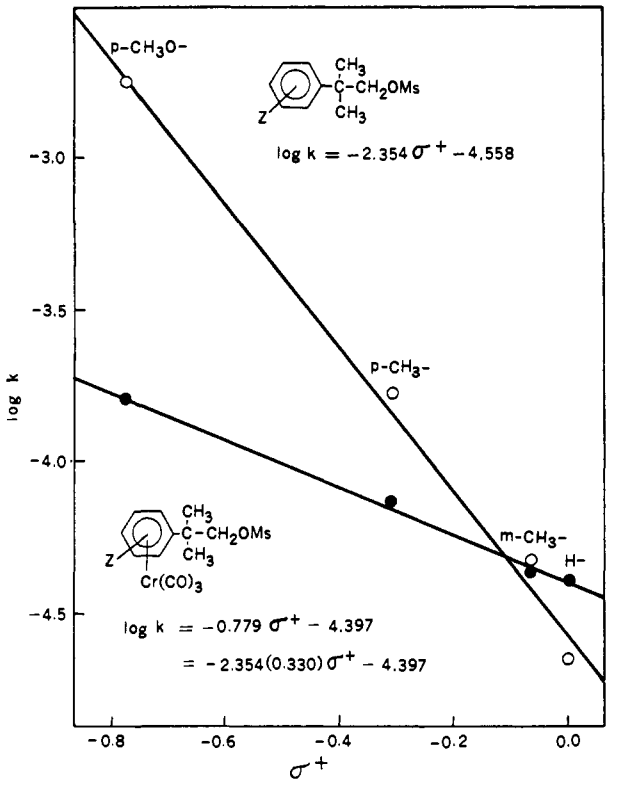
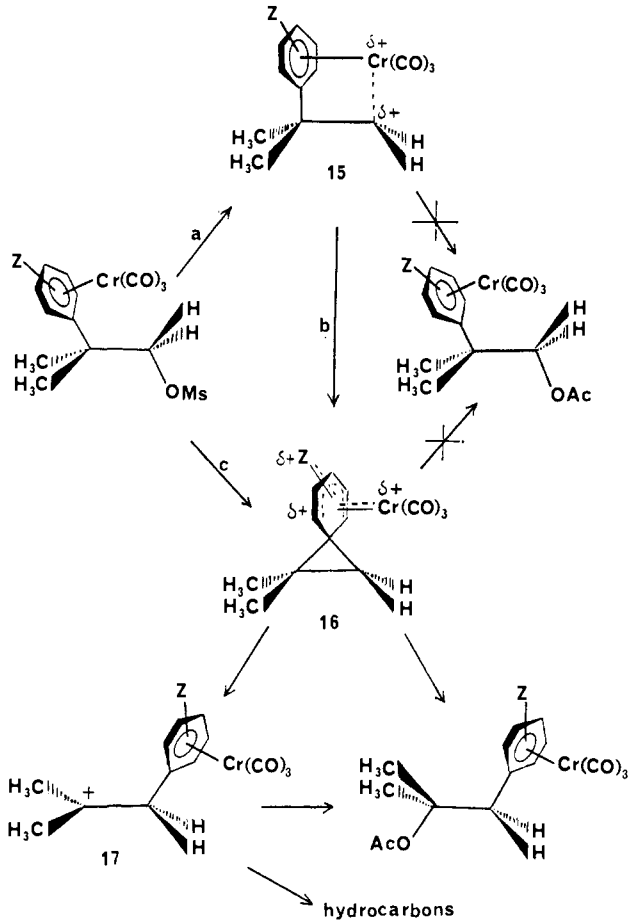


Figure 1. Modified Hammett plot for the acetolysis rate constants at 75° of complexed (●) and noncomplexed (○) 2-aryl-2-methyl-1-propyl methanesulfonates.

barring drastic changes in reaction mechanism,[38] the differences in slope of the complexed and noncomplexed series of compounds are due primarily to an attenuation effect by the π-bonded metal upon the substituent constant (σ^+) of the σ-bonded group which arises because the latter is effectively attached in the complex to a larger "electron sink," *i.e.*, to a more extensive conjugated system.[40]

Our results in these 2-[π-(aryl)chromium tricarbonyl]-2-methyl-1-propyl cases do not permit us to distinguish between the d-orbital bridging and "σ–π-type delocalization" mechanisms considered earlier[2] and depicted, paths ab and c, respectively, for the solvolysis of 2-[π-(aryl)chromium tricarbonyl]-2-methyl-1-propyl methanesulfonates in Chart IV.[41] Either would appear to accommodate the observed rate enhancements, for electron-donating substituents on the aromatic ring of a π-(arene)chromium tricarbonyl are known to increase the electron density on the metal,[42] and hence would be

Chart IV



expected to increase the rate of either step a or step c. Attenuation effects similar to those observed would be expected whether chromium or aryl bridging were important. Since the solvolysis of a neophyl-type derivative is known already to involve minimal backside nucleophilic participation by the solvent,[43] the lower acetate *b* value for the complex **1a**-OMs, if it is experimentally significant, may imply that the initial ion pair is less stable and hence that front side displacement is less important in this case.[2] This is understandable in view of the more extensive charge delocalization expected for the complexed cations **15** and/or **16**.

The larger rate enhancements observed in these neophyl-type complexes relative to the 3-phenyl-2-butyl reflect the fact that participation is more important at a primary than at a secondary center.[43] That these unsymmetrically substituted 2-phenyl-2-methyl-1-propyl (neophyl-type) complexes yield aryl-migrated products exclusively whereas the "symmetric"[44] 3-phenyl-2-butyl complexes solvolyzed previously exhibit no aryl migration under similar conditions is testimony to the greater stability of the rearranged tertiary cation **17**, and to the

(38) It does not appear to have been definitely established for example that the hydrolyses of chromium tricarbonyl-complexed methyl benzoates[16] occur with acyl- rather than alkyl- oxygen cleavage, *i.e.*, are $B_{AC}2$ rather than $B_{AL}2$.[39] Of course if π-complexation does alter the reaction course the reaction constants could differ appreciably.

(39) *Cf.* E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 315, 342.

(40) The effect may be compared to the loss of substituent additivity which is sometimes observed in the solvolyses of *p,p'*-disubstituted benzhydryl derivatives; *cf.* (a) J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964); and (b) S. Nishida, *J. Org. Chem.*, **32**, 2695 (1967).

(41) We do not intend in Chart IV to indicate whether **15**, **16**, and **17** are intermediates or transition states as we do not feel that our present data permit us to make this distinction. It is likely that the initial intermediate, be it **15**, **16**, or **17**, is an ion pair. The product-forming intermediate could be **16** and/or **17**.

(42) (a) E. O. Fischer and S. Schreiner, *Chem. Ber.*, **92**, 938 (1959); (b) R. D. Fischer, *ibid.*, **93**, 165 (1960); (c) D. A. Brown and H. Sloan, *J. Chem. Soc.*, 3849 (1962); (d) W. Strohmeier and H. Hellmann, *Ber. Bunsenges. Phys. Chem.*, **67**, 190 (1963); (e) W. Strohmeier and H. Hellmann, *Chem. Ber.*, **97**, 1877 (1964); (f) W. Strohmeier and H. Hellmann, *Ber. Bunsenges. Phys. Chem.*, **69**, 178 (1965); (g) D. A. Brown and D. G. Carroll, *J. Chem. Soc.*, 2822 (1965); (h) D. A. Brown and J. R. Raju, *J. Chem. Soc., A*, 1617 (1966); (i) W. Strohmeier, G. Popp, and J. F. Guttenberger, *Chem. Ber.*, **99**, 165 (1966).

(43) *Cf.* (a) M. G. Jones and J. L. Coke, *J. Amer. Chem. Soc.*, **91**, 4284 (1969); (b) A. F. Diaz and S. Winstein, *ibid.*, 4300 (1969), and references cited therein.

(44) (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); (b) H. C.Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

increased π-arylchromium tricarbonyl participation which its formation induces.[31,45]

Experimental Section[46]

Preparation of 2-Phenyl-2-methylpropanol (1-OH). The procedure of Whitmore, *et al.*,[3a] was followed: bp 89–90° (2.5 mm) [lit.[3a] 131° (30 mm)]; ir (neat) 3370 (OH); 3090, 3060, 3020 (CH phenyl); 2960, 2920, 2870 (CH aliphatic); 1605, 1500 (phenyl nucleus); 1470, 1390, 1380 (>C(CH_3)$_2$); 1035 (CO); 760, 697 cm^{-1} (monosubstituted phenyl);[47] nmr (CCl_4) δ 7.22, multiplet (C_6H_5–), 3.40, singlet (≻CCH_2O–), 2.41, singlet (–OH–), 1.22, singlet (>C(CH_3)$_2$).

Preparation of 2-*p*-Anisyl-2-methylpropanol (2-OH). The procedure of Winstein and Heck[3b] was followed: mp 37–42° [lit.[3b] mp 45–46.5°]; ir ($CHCl_3$) 3610, 3560, 3450 (OH); 3100, 3050, 3025, 3000 (CH phenyl); 2960, 2930, 2900, 2870 (CH aliphatic); 2830 (OCH_3); 1615, 1590, 1520 (phenyl nucleus); 1470, 1380, 1375 (>C(CH_3)$_2$); 833 cm^{-1} (*para*-disubstituted phenyl);[47] nmr (CCl_4) δ 7.09, 6.97, 6.66, 6.50, AB quartet, $J \approx 8$ Hz (–$C_6H_2^AH_2^B$–); 3.62, singlet (CH_3O–); 3.30, singlet (≻CCH_2O–); ~2.15, broad singlet (–OH); 1.12 singlet (>C(CH_3)$_2$).

Preparation of 2-*p*-Tolyl-2-methylpropanol (3-OH). The procedure of Whitmore *et al.*,[3a] was followed: bp 91° (1 mm) [lit.[3c] bp 87–88° (1.5 mm)]; ir (CCl_4) 3640, 3580, 3450 (OH); 3090, 3050, 3020 (CH phenyl); 2960, 2920 (CH aliphatic); 2830 (CH_3); 1625, 1505 (phenyl nucleus); 1480, 1395 (>C(CH_3)$_2$); 1044 cm^{-1} (C–O);[47] nmr (CCl_4) δ 7.21, 7.07, 7.03, 6.89, AB quartet, $J \approx 8$ Hz (–$C_6H_2^AH_2^B$–); 3.33, singlet (≻CCH_2O–); ~2.60, singlet (–OH); 2.28, singlet ($CH_3C_6H_4$–); 1.20, singlet (>C(CH_3)$_2$).

Preparation of 2-*m*-Tolyl-2-methylpropanol (4-OH). The procedure of Winstein and Heck[3c] was followed: ir ($CHCl_3$) 3610, 3570, 3440 (OH); 3000 (CH phenyl); 2955, 2920, 2865 (CH aliphatic); 1605, 1590, 1480 (phenyl nucleus); 1370, 1375 (>C(CH_3)$_2$); 1035 cm^{-1} (CO);[47] nmr (CCl_4) δ ~6.95, multiplet (–C_6H_4–); 3.40, broad perturbed singlet (?) (≻CCHHO–); 2.30, singlet (–C_6H_4–CH_3); ~1.5 broad singlet (–OH); 1.22, singlet (>C(CH_3)$_2$).

Preparation of the Methanesulfonates. The methanesulfonates **1–4**-OMs were prepared as reported previously.[2] Melting points and yields are listed in Table III.

Table III. Melting Points and Yields of the 2-Aryl-2-methylpropyl Methanesulfonates

Compd	Mp, °C	Yield, %
1-OMs	26.1–26.3	69.6
2-OMs	70–71	89.5
3-OMs	57.5–58.5	59.1
4-OMs	<20[a]	70.8

[a] Purified by recrystallization from ether–pentane at <10°.

2-Phenyl-2-methylpropyl Methanesulfonate (1-OMs). Ir analysis showed ($CHCl_3$) 3080, 3060 (CH phenyl); 3020, 2970, 2930 (CH aliphatic); 1610, 1500 (phenyl nucleus); 1360, 1163 (OSO_2); 697 cm^{-1} (monosubstituted phenyl);[47] nmr (CCl_4) δ 7.28, broad singlet (C_6H_5–); 4.10, singlet (≻CCH_2O–); 2.63, singlet (–OSO_2CH_3); 1.36, perturbed singlet (>C(CH_3)$_2$).

Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.86; H, 7.06; S, 14.05. Found: C, 58.07; H, 7.11; S, 13.75.

2-*p*-Anisyl-2-methylpropyl Methanesulfonate (2-OMs). Ir analysis showed ($CHCl_3$) 3100 (sh), 3010, 2970, 2935, 2905, 2875 (CH); 2840 (OCH_3); 1620, 1590, 1520 (phenyl nucleus); 1360, 1170 (OSO_2); 831 cm^{-1} (*para*-disubstituted phenyl);[47] nmr (CCl_4) δ 7.23, 7.10, 6.80, 6.67, AB quartet, $J \approx 8$ Hz (–$C_6H_2^AH_2^B$–); 4.08, singlet (≻CCH_2O–); 3.72, singlet (CH_3O–); 2.72, singlet (–OSO_2CH_3); 1.38, singlet (>C(CH_3)$_2$).

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.79; H, 7.02; O, 24.77; S, 12.41. Found: C, 55.80; H, 6.84; O, 24.61; S, 12.29.

2-*p*-Tolyl-2-methylpropyl Methanesulfonate (3-OMs). Ir analysis showed ($CHCl_3$) 3080, 3030, 2970, 2930 (CH); 2870 (CH_3); 1360, 1180 cm^{-1} (OSO_2);[47] nmr (CCl_4) δ 7.30, 7.16, 7.11, 6.97, AB quartet, $J \approx 9$ Hz (–$C_6H_2^AH_2^B$–); 4.08, singlet (≻CCH_2O–); 2.65, singlet (–OSO_2CH_3); 2.29, singlet ($CH_3C_6H_4$–); 1.34, singlet (>C(CH_3)$_2$).

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49; O, 19.81; S, 13.23. Found: C, 59.39; H, 7.29; O, 19.90; S, 13.09.

2-*m*-Tolyl-2-methylpropyl Methanesulfonate (4-OMs). Ir analysis showed ($CHCl_3$) 3020, 2970, 2930, 2910 (CH); 2870 (CH_3); 1610, 1590, 1470 (phenyl nucleus); 1360, 1170 cm^{-1} (OSO_2);[47] nmr (CCl_4) δ ~7.00, multiplet (–C_6H_4–); 4.02, singlet (≻CCH_2O–); 2.61, singlet (–OSO_2CH_3); 2.29 ($CH_3C_6H_4$–); 1.37, singlet (>C(CH_3)$_2$).

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49; O, 19.81; S, 13.23. Found: C, 59.47; H, 7.49; O, 19.69; S, 13.09.

Preparation of the π-Complexed Methanesulfonates. The methanesulfonates **1a–4a**-OMs were prepared by the reaction of chromium hexacarbonyl with **1–4**-OMs in a Strohmeier apparatus[48] as described previously.[2] The yields and melting points are summarized in Table IV.

Table IV. Melting Points and Yields of the π-Complexed Methanesulfonates

Compd	Mp, °C	Yield, %
1a-OMs	71–72	66.0
2a-OMs	108.5–110	26.8
3a-OMs	79–80	73.8
4a-OMs	82–84	72.7

2-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (1a-OMs). Ir analysis showed ($CHCl_3$) 3020, 2940, 2900 (CH); 1970, 1900 (C≡O); 1370, 1170 (OSO_2); 660, 631, 530 cm^{-1} (CrC);[47] nmr ($CDCl_3$) δ 5.68–5.10, multiplet (C_6H_5–); 4.12, singlet (≻CCH_2O–); 2.99, singlet (–OSO_2CH_3); 1.41, singlet (>C(CH_3)$_2$); uv (C_2H_5OH) 224 mμ (ε 18,000), 251 (5900), 317 (8400).

Anal. Calcd for $C_{15}H_{16}O_6SCr$: C, 46.15; H, 4.43; S, 8.80; Cr, 14.27. Found: C, 46.27; H, 4.50; S, 8.60; Cr, 14.03.

2-[π-(*p*-Anisyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (2a-OMs). Ir analysis showed ($CHCl_3$) 3110, 3020, 2980, 2940 (CH); 1975, 1875 (C≡O); 1375, 1170 (OSO_2); 825 (*para*-disubstituted phenyl); 671, 626, 520 cm^{-1} (CrC);[47] nmr ($CDCl_3$) δ 5.73, 5.61, 5.12, 5.00, AB quartet, $J \approx 7.5$ Hz (–$C_6H_2^AH_2^B$–); 4.08, singlet (≻CCH_2O–); 3.75, singlet (CH_3O–); 3.01, singlet (–OSO_2CH_3); 1.36, singlet (>C(CH_3)$_2$); uv (C_2H_5OH) 214 mμ (ε 22,917), 317 (7042).

Anal. Calcd for $C_{12}H_{18}O_7SCr$: C, 45.69; H, 4.60; O, 28.40; S, 8.13. Found: C, 45.56; H, 4.55; O, 28.25; S, 7.93.

2-[π-(*p*-Tolyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (3a-OMs). Ir analysis showed ($CHCl_3$) 3030 (CH phenyl); 2980, 2940 (CH aliphatic); 1980, 1900 (C≡O); 1370, 1170 (OSO_2); 660, 625, 530 cm^{-1} (CrC);[47] nmr ($CDCl_3$) δ 5.80, 5.69, 5.30, 5.19, AB quartet, $J = 7$ Hz (–$C_6H_2^AH_2^B$–); 4.22, singlet (≻CCH_2O–); 3.12, singlet (–OSO_2CH_3); 2.36, singlet ($CH_3C_6H_4$–); 1.49, singlet (>C(CH_3)$_2$); uv (C_2H_5OH) 218 mμ (ε 21,900), 254 (5100), 318 (7300).

Anal. Calcd for $C_{15}H_{18}O_6SCr$: C, 47.62; H, 4.79; O, 25.37; S, 8.47. Found: C, 47.70; H, 4.89; O, 25.27; S, 8.38.

2-[π-(*m*-Tolyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (4a-OMs). Ir analysis showed ($CHCl_3$) 3050, 3025, 2975, 2940, 2880 (CH); 1970, 1900 (C≡O); 1370, 1168 (OSO_2); 830, 745, 730 (phenyl); 682, 656, 627 cm^{-1} (CCr);[47] nmr ($CDCl_3$) δ 5.33, singlet (–C_6H_4–); 4.13, singlet (≻CCH_2O–); 3.02, singlet (–OSO_2CH_3); 2.26, singlet ($CH_3C_6H_4$–); 1.48, singlet (>C(CH_3)$_2$).

Anal. Calcd for $C_{15}H_{18}O_6SCr$: C, 47.62; H, 4.80; O, 25.37; S, 8.47. Found: C, 47.53; H, 4.68; O, 25.30; S, 8.36.

The acetolysis rates were measured titrimetrically using the ampoule technique described previously.[2] With the complexed mate-

(45) *Cf.* C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4289 (1969); (b) P. von R. Schleyer and C. J. Lancelot, *ibid.*, 4297 (1969), and references cited therein.

(46) Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrophotometer, Model 337, on a Model 202 ultraviolet spectrometer, and on a Varian A-60A nmr spectrometer. Tetramethylsilane (δ 0.00) and/or chloroform (δ 7.31) were employed as internal standards in the latter case. Gas chromatographic analyses were carried out in an F & M Model 500 chromatograph equipped with a hot-wire detector. Columns employed were 8, 12, and 16 ft × 0.25 in. coiled copper tubes packed with 20% Carbowax 20M on 60–80 mesh Chromosorb CL.

(47) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(48) W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).

rials the following deoxygenation procedure was employed. Dry oxygen-free[49] nitrogen was passed through the sodium acetate-containing rate solvent[2,50] at 60–70° for ~10 min. The solution was cooled and stored under an oxygen-free nitrogen atmosphere. Prior to each run oxygen-free nitrogen was passed through the individual ampoules at 25°. The tubes were then sealed and wrapped in aluminum foil to protect them from light during the kinetic determinations.

One rate run was carried out using a more rigorous deoxygenation procedure. The methanesulfonate **1a**-OMs (0.342 g, 0.937 mmol) was added to 50 ml of 0.0476 *M* sodium acetate solution in deoxygenated acetic acid (*vide supra*). Nine 5-ml aliquots of the solution were pipetted into ampoules, the ampoules were attached to a vacuum manifold and cooled to −80°. The system was evacuated to ~0.1 mm and allowed to warm to room temperature. After repeating the freeze-thaw cycle three times, the pressure was increased to ~600 mm by introducing dry oxygen-free nitrogen.[49] The ampoules were sealed and the reaction rate determined at 87.45 ± 0.02° as described previously.[2] The first-order rate constant was found to be 0.000141 sec^{-1} compared to the 0.000142 sec^{-1} observed earlier. Because of the close agreement between the two determinations, the freeze–thaw technique was not used in subsequent runs.

Acetolysis Products of 2-Phenyl-2-methylpropyl Methanesulfonate (1-OMs). Run A. To a 10-ml portion of 0.0468 *M* sodium acetate in anhydrous acetic acid[50] was added 0.0482 g (0.212 mmol) of the methanesulfonate. The solution was allowed to react for 24 hr (ten half-lives) at 87°, cooled, poured over ~75 ml of crushed ice, and extracted with three 25-ml portions of pentane. The combined extract was washed twice with excess cold saturated sodium carbonate solution, twice with cold water, and dried over anhydrous magnesium sulfate. The solution was filtered, and the filtrate was concentrated to ~10 ml by slow distillation of the pentane through a 12 in. wire-spiral-packed, vacuum-jacketed column. The products were then treated with excess lithium aluminum hydride. Analysis by glpc on the 16-ft Carbowax column at 145° revealed the presence of three components whose retention times (in minutes) and relative peak areas were 4.1 (44.7%), 5.9 (28.9%) and 20.6 (26.4%). In a duplicate **run B** the relative areas were 45.5, 29.2, and 25.3%, respectively. Analysis by glpc showed no peak with a retention time corresponding to that of authentic **1**-OH. The two runs were combined and the products collected for spectral examination.

The **first component** exhibited nmr (CCl_4) δ 7.12, singlet (C_6H_5–); 4.73, broad singlet (>C=C*HH*); 3.28, singlet ($C_6H_5CH_2C$(–)=C<); 1.67, singlet (–C(CH_3)=C<). The infrared spectrum is identical with that of authentic 3-phenyl-2-methylpropene (**6**).[61a]

The **second component** exhibits ir[51b] and nmr[52] spectra which are identical with those of authentic 1-phenyl-2-methylpropene (**9**).

The **third component** is identical with 1-phenyl-2-methyl-2-propanol (**12-OH**)[3c,5] obtained by the reaction of methylmagnesium iodide with ethyl phenylacetate.

Acetolysis Products of 2-*p*-Anisyl-2-methylpropyl Methanesulfonate (2-OMs). Run C. A solution of 50 mg (0.19 mmol) of **2**-OMs in 10 ml of acetic acid[50] buffered with 0.0496 *M* sodium acetate was heated at 87° for 21 min (10 half-lives). The products were isolated as described for run A except that a 50:50 ether–pentane mixture (instead of pure pentane) was used for the extraction. Analysis on the 12-ft Carbowax column at 175° showed the presence of three components whose retention times (minutes) and relative peak areas were 5.0 (44%), 7.2 (31%) and 21.0 (25%).

The **first component** had ir (CCl_4) 3070, 3025, 3000, 2970, 2950, 2935, 2905, 2830 (CH); 1660 (C=C) 1620, 1595, 1520 (phenyl nucleus), 840 (*para*-disubstituted phenyl), 890 cm^{-1} (=CH_2, terminal);[47] nmr (CCl_4) δ 7.01, 6.87, 6.72, 6.58, AB quartet, J = 8 Hz ($-C_6H_2^AH_2^B$–); 4.67, broad singlet (>C=C*HH*); 3.70, singlet (CH_3O–); 3.20, singlet ($-C_6H_4CH_2C$(–)=C<); 1.67, singlet (–C(CH_3)=C<). This component is 3-*p*-anisyl-2-methylpropene (**7**).[63]

The **second component** had ir (CCl_4) 3080, 3050, 2995, 2960, 2950, 2925, 2905, 2850, 2830 (CH); 1675 (C=C); 1620, 1580, 1520 (phenyl nucleus); 1395, 1390 (>C(CH_3)$_2$); 865, 850 cm^{-1} (>C=CH– and *para*-disubstituted phenyl).[47] The nmr spectrum is identical with that of 1-*p*-anisyl-2-methylpropene (**10**).[52]

The **third component** had ir (CCl_4) 3960, 3670, 3450 (OH); 3080, 3050, 3020, 2990 (CH phenyl) 2960, 2920, 2900, 2850 (CH aliphatic); 2825 (OCH_3); 1620, 1590, 1520 (phenyl nucleus); 1390, 1380 (>C(CH_3)$_2$); 845, 835 cm^{-1} (*para*-disubstituted phenyl);[47] nmr (CCl_4) δ 7.36, 7.22, 7.03, 6.89, AB quartet, J = 8 Hz ($-C_6H_2^AH_2^B$–); 4.04, singlet (CH_3O–); 2.90, singlet ($-C_6H_4CH_2C$<); ~1.78, broad singlet (O*H*); 1.45, singlet (>C(CH_3)$_2$). This component is 1-*p*-anisyl-2-methyl-2-propanol (**13-OH**).[54]

Acetolysis Products of 2-*p*-Tolyl-2-methylpropyl Methanesulfonate (3-OMs). Run D. A solution of 27.2 mg (0.0720 mmol) of **3**-OMs in 5 ml of acetic acid[50] buffered with 0.0468 *M* sodium acetate was allowed to react for 4.4 hr (10 half-lives) at 85°. Products were isolated as described for run A. A glpc analysis on the 8-ft Carbowax column at 135° showed the presence of three components with retention times (minutes) and peak areas of 2.8 (43.6%), 4.2 (34.2%), and 14.4 (22.2%). In a duplicate **run E** the relative peak areas were 41.8, 34.4, and 23.8, respectively.

The **first component** had ir (CCl_4) 3080, 3050, 3020, 3000, 2970, 2920 (CH); 1650, 1520 (C=C and phenyl nucleus); 890 (C=CH_2); 840, 832 cm^{-1} (*para*-disubstituted phenyl);[47] nmr (CCl_4) δ 6.85, singlet ($-C_6H_4$–); 4.63, broad singlet (>C=C*HH*); 3.16, singlet ($-C_6H_4CH_2C$(–)=C<); 2.21, singlet ($-C_6H_4CH_3$); 1.59, singlet (–C(CH_3)=C<). This compound is 3-*p*-tolyl-2-methylpropene (**8**).[53]

The **second component** had ir (CCl_4) 3125, 3080, 3040, 3020, 2970, 2920, 2850 (CH); 1640, 1520 (C=C and phenyl nucleus); 1390, 1380 (>C(CH_3)$_2$); 862, 842 cm^{-1} (>C=CH– and *para*-disubstituted phenyl).[47] The nmr spectrum is identical with that of 1-*p*-tolyl-2-methylpropene (**11**) published by previous workers.[52]

The **third component** had ir (CCl_4) 3580, 3450 (OH); 3175, 3080, 3060, 3020, 3000 (CH phenyl); 2970, 2920, 2870 (CH aliphatic); 1520 (phenyl nucleus); 1385, 1375 (>C(CH_3)$_2$); 1130 cm^{-1} (C—O); nmr (CCl_4) δ 6.88, singlet ($-C_6H_4$–); 2.58, singlet ($-C_6H_4CH_2C$<); 2.23, singlet ($-C_6H_4CH_3$); 2.07, singlet (–O*H*); 1.10, singlet (>C(CH_3)$_2$). This compound is 1-*p*-tolyl-2-methyl-2-propanol (**14**-OH).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.29; H, 9.91.

Acetolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (1a-OMs). Run F. To 10 ml of a solution of 0.0486 *M* sodium acetate in deoxygenated acetic acid[2,50] was added 73.5 mg (0.201 mmol) of **1a**-OMs. The solution was sealed in an ampoule under nitrogen, protected from light and heated at 87° for 14.6 hr (10 half-lives). The solution was poured over ice and extracted with three 25-ml portions of a 1:1 pentane–ether mixture. The combined extracts were washed in succession with excess cold saturated sodium carbonate, and twice with cold water. The yellow pentane solution was then treated with a saturated solution of ceric ammonium nitrate in acetone[55] until no yellow color was observed. The colorless organic solution was washed four times with cold water, dried over anhydrous magnesium sulfate, and reduced with lithium aluminum hydride. Analysis by glpc on the 16-ft Carbowax column at 155° revealed the presence of four components. Retention times and peak areas were 3.2 (32.0%), 4.8 (10.3%), 16.8 (57.7%), and 30.0 (trace). In a duplicate **run G**, the relative areas were 31.3, 11.0, 57.7%, and a trace.

The **first, second, and third components** were identified as **6**, **9**, and **12-OH**, respectively, by comparison of their infrared spectra with those of authentic samples.

The **fourth component** has a glpc retention time identical with that of authentic **1**-OH.

Acetolysis Products of 2-[π-(*p*-Anisyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (2a-OMs). Run H. The acetolysis was performed using the procedure described for **1a**-OMs (run F). A solution of 50 mg (0.13 mmol) of **2a**-OMs in 10 ml of 0.0496 *M* sodium acetate in deoxygenated acetic acid was heated at 87° for 3.7 hr (10 half-lives). A glpc analysis of the decomplexed and reduced product mixture on the 16-ft Carbowax column at 160° showed the presence of two components with a relative abundance of 51.4 and 48.6%, respectively. The **first component** was identical in all respects with the hydrocarbon **7**, the **second component** with alcohol **13**-OH (*cf.* run C).

(49) L. F. Fieser, *J. Amer. Chem. Soc.*, **46**, 2639 (1924).
(50) Prepared by distilling reagent grade acetic acid from acetic anhydride and adding ~1% acetic anhydride.[2]
(51) (a) Sadtler Standard Spectra, Infrared No. 2046; (b) No. 2045.
(52) H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965).
(53) C. Rüchardt, *Chem. Ber.*, **94**, 2609 (1961).
(54) S. Winstein and E. Hedaya, *J. Amer. Chem. Soc.*, **89**, 1661 (1967).
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Acetolysis Products of 2-[π-(p-Tolyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (3a-OMs). Run I. The acetolysis was performed as described for **1a**-OMs (run F) using 0.192 g (0.508 mmol) of **3a**-OMs in 25 ml of 0.0468 *M* sodium acetate in deoxygenated acetic acid. The products were isolated after 9.7 hr (10 half-lives). A glpc analysis on the 16-ft Carbowax column at 160° showed the presence of three components, relative abundance 23.1, 7.9, and 69.0%. In a duplicate **run J** the relative abundance of the products was 22.1, 9.2, and 68.7%, respectively. In addition a trace of product whose retention time was identical with that of authentic **3a**-OH could be detected. The three major components were collected and identified as **8**, **11**, and **14**-OH, respectively, by comparison of their infrared spectra with those of authentic samples (see run D).

Complexed Products from the Acetolysis of 2-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (1a-OMs). Run K. To 75 ml of a solution of 0.0468 *M* sodium acetate in deoxygenated acetic acid was added 0.558 g (1.53 mmol) of **1a**-OMs. The solution was sealed under nitrogen in an ampoule and heated in the dark at 87° for 14.6 hr (10 half-lives). After the solution had cooled, it was poured over ice and extracted with three 50-ml portions of a 1:1 pentane–ether mixture. The extracts were combined and washed twice with excess cold saturated sodium carbonate, twice with cold water, and dried over anhydrous magnesium sulfate. The volume of the solution was reduced to 5 ml by slow distillation of the solvent. Products were chromatographed over neutral alumina (Woelm, activity grade I). Two yellow bands were observed. The first was eluted with a 1:5 ether–pentane mixture, the second with a 4:1 ether–pentane mixture.

Products from the **first band** were isolated by evaporating the solvent at reduced pressure (20 mm). A 0.0753-g sample (19.0%) of a yellow oil remained which consisted of ~75% 3-[π-(phenyl)-chromium tricarbonyl]-2-methylpropene (**6a**) and 25% 1-[π-(phenyl)-chromium tricarbonyl]-2-methylpropene (**9a**): nmr (CCl_4) δ 5.77, broad singlet (~0.25 $C_6H_5CH{=}C<$ of **9a**); 5.11, broad singlet (C_6H_5– of **6a** + **9a**); 4.70, broad singlet (~1.5 $>C{=}CH_2$ of **6a**); 2.98, singlet (~1.5 $C_6H_5CH_2(-){=}C<$ of **6a**); 1.85, broad singlet partly overlapping a broad singlet at 1.73 (~3.75 $-C(CH_3){=}CH_2$ of **6a** + $>C{=}C(CH_3)_2$ of **9a**).

The product obtained from the **second band** crystallized from pentane to give 0.174 g (35.6%) of a yellow solid: mp 92–93°; ir (CH_2Cl_2) 3060, 2980, 2940 (CH); 1970, 1890 (C≡O); 1740 (ester C=O); 1390, 1375 ($>C(CH_3)_2$); 1250 (CO); 663, 635, 536 cm^{-1} (CrC);[47] nmr ($CDCl_3$) δ 5.41, multiplet (C_6H_5–); 2.77, singlet (C_6H_5–$CH_2C<$); 2.02, singlet ($-OCOCH_3$); 1.55, singlet ($>C(CH_3)_2$). On the basis of the nmr spectrum, this compound has been assigned the structure of 2-methyl-1-[π-(phenyl)chromium tricarbonyl]-2-propyl acetate (**12**-OAc).

Anal. Calcd for $C_{15}H_{16}CrO_5$: C, 54.88; H, 4.91. Found: C, 55.06; H, 5.03.

Complexed Products from the Acetolysis of 2-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (1a-OMs) at One Half-life. Run L. A solution of 0.739 g (2.03 mmol) of the methanesulfonate in 75 ml of deoxygenated acetic acid[50] buffered with 0.0468 *M* sodium acetate was heated at 87° for 1.5 hr (1 half-life). The products were isolated as described in run K. Three bands were observed. The **first band** was eluted with a 1:9 ether–pentane mixture. Evaporation of the solvent at reduced pressure gave 75 mg (14%) of a yellow oil which consisted of a mixture of the olefins **6a** and **9a**. The **second band** was eluted with a 4:1 ether–pentane mixture and yielded, after removal of the solvent, 127 mg (19.7%) of the acetate **12**-OAc (*cf.* run K). The **third band** was eluted with a 1:9 acetone–ether mixture and yielded after evaporation of the solvent and recrystallization from a 1:1 ether–pentane mixture 192 mg (25.9%) of the starting methanesulfonate **1a**-OMs.

The Stability of π-Complexed Olefins to the Acetolysis and Isolation Procedures. Run M. To a solution of 0.0468 *M* sodium acetate in 10 ml of anhydrous deoxygenated acetic acid was added 76 mg (0.30 mmol) of the π-complexed olefin mixture (**6a** + **9a**) from run K. The solution was heated at 87° for 14.6 hr and the products were isolated as described for **run F**. A glpc analysis showed the presence of two components with relative peak areas of 74.8 and 25.2%. The retention times on the 16-ft Carbowax column at 145° were identical with those of **6** and **9**, respectively.

The Stability of 1-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Acetate (12a-OAc) to the Acetolysis and Isolation Procedures. Run N. To a solution of 0.0468 *M* sodium acetate in 5 ml of anhydrous deoxygenated acetic acid was added 35 mg (0.11 mmol) of **12**-OAc. The mixture was heated at 87° for 14.7 hr and the products were isolated as described for **run F**. A glpc analysis on the 16-ft Carbowax column at 155° showed a single component whose retention time was identical with **12**-OH.

Formolysis Products of 2-[π-(Phenyl)chromium tricarbonyl]-2-methylpropyl Methanesulfonate (1a-OMs). Run R. To a solution of 0.0575 *M* sodium formate in deoxygenated formic acid (Matheson Coleman and Bell >97% pure) was added 77 mg (0.21 mmol) of **1a**-OMs. The solution was sealed under nitrogen and heated at 70° for 0.5 hr (greater than 10 but less than 30 half-lives). The products were isolated as described for run F and analyzed by glpc on the 16-ft Carbowax column. Three components were found to be present with the relative abundance of 4.8, 3.1, and 92.1%. After collection and comparison of the ir spectra with known materials the products were identified as **6**, **9**, and **12**-OH, respectively.

[π-(Phenyl)chromium tricarbonyl]acetic acid was prepared by the alkaline hydrolysis of the corresponding methyl ester:[11] ir ($CHCl_3$) 3400–3100 (OH, bonded); 3010, 2950 (CH); 1980, 1905 (C≡O); 1720 cm^{-1} (C=O); nmr ($CDCl_3$) ~5.36, broad singlet (C_6H_5–); 3.46, singlet ($C_6H_5CH_2CO$–). The infrared spectrum at high dilution was determined on a Perkin-Elmer Model 621 spectrophotometer in 0.005 *M* solutions of the complexed acid in chloroform or deuteriochloroform using 1-cm quartz cells.[56] A nonbonded hydroxyl peak was evident at 3509 cm^{-1}, but no hydrogen bonded OH absorptions were found in the 3000–2500-cm^{-1} region. Under identical conditions noncomplexed phenylacetic acid shows a free OH absorption of comparable magnitude at 3516 cm^{-1}. Both the complexed and noncomplexed acids show a weak and very broad absorption at 3300–3100 cm^{-1}, probably due to the presence of the corresponding dimer.[57]

Acknowledgment. The bulk of this work was supported by the Directorate of Chemical Sciences of the Air Force Office of Scientific Research, Grant No. 991-66. It was supported briefly during its initial stages by the National Science Foundation, Grant GP-224. We are indebted to each of these agencies for their generous backing.

(56) We thank Dr. James R. Durig and Mr. James N. Willis for their help in this determination.

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