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THE PREPARATION AND ACETOLYSIS OF SOME [π-PHENYLCHROMIUM TRICARBONYL]BENZYL *p*-TOLUENESULFONATES AND THEIR NONCOMPLEXED ANALOGS. A SEARCH FOR σ—π DELOCALIZATION *

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Summary

The substituted benzyl tosylates *p*-phenyl, *p*-(π-phenylchromium tricarbonyl), *p*-(*p*'-nitrophenyl), *m*-phenyl, *m*-(π-phenylchromium tricarbonyl) and *m*-(*p*'-nitrophenyl) have been prepared and their solvolysis rates in buffered and/or unbuffered acetic acid determined. At 69.0°C their reactivities relative to benzyl tosylate (1.00) are: 10.8, 7.14, 0.742, 0.571, 0.134 and 0.173, respectively. Conjugative substituent parameters are calculated at 69°C for *p*-nitrophenyl (σ_m^+ 0.221, σ_p^+ 0.060) and π-phenylchromium tricarbonyl (σ_m^+ 0.262, σ_p^+ —0.144). The ability of α-(π-phenylchromium tricarbonyl) to stabilize electrophilic centers is compared with that of α-ferrocenyl and mechanisms of electron donation are discussed.

Introduction

Some organometallic π-complexes stabilize carbonium ions when directly bonded to the electron deficient center. Metallocenyl [1—7] π-cyclobutadienyliron tricarbonyl [8], π-phenylchromium tricarbonyl [9,10] and possibly π-cyclopentadienylmanganese tricarbonyl [4b,11] act in this manner. The phenomenon was first observed in ferrocenylcarbinyl derivatives and has been most extensively investigated in this system [1]. Generally speaking, two alternate modes of electron donation from the ferrocenyl moiety to the electron-deficient carbon have been proposed. Richards and Hill [2a—c] suggest that the metal acts as a sort of "neighboring group" and shares *d*-electrons directly with the plus-charged carbon. Alternately, Traylor and coworkers [5] ascribe the stabilization to a

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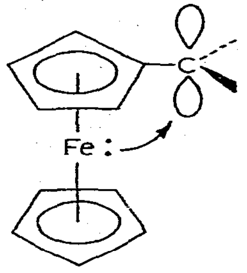
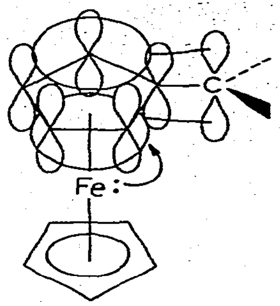
* Portions of this work were presented at the 162nd National Meeting of the American Chemical Society, Washington, D.C. September 1971, Abstract ORGN 011.

resonance type interaction transmitted via the cyclopentadienyl ring. These interaction mechanisms, which we will refer to as "*d*-orbital bridging" and "σ—π delocalization" [5e], respectively, are depicted schematically.

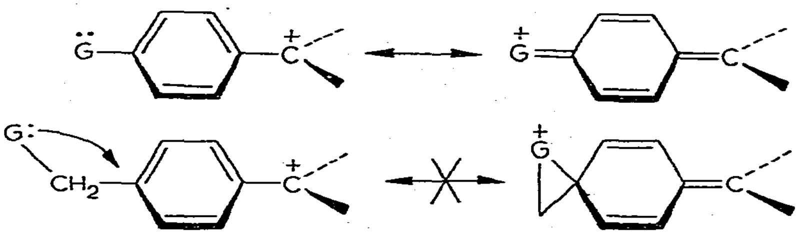


d-orbital bridging

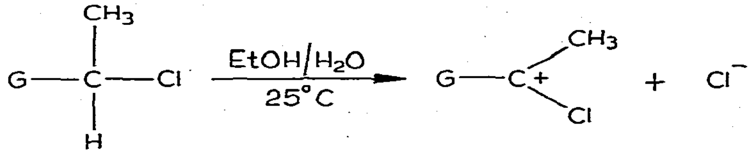


σ—π delocalization

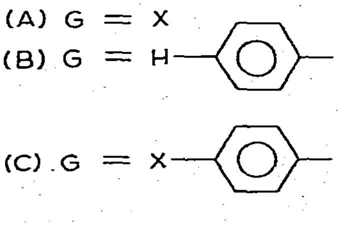
Many attempts have been made to distinguish experimentally between these two possibilities [1,2d,e, 4—6]. Although the question is not yet completely resolved the most detailed analysis of chemical evidence has probably been provided by Traylor and Ware [5a,e]. They reasoned that *p*-phenylene would transmit a purely resonance effect such as σ—π delocalization, but should inhibit stabilization when interposed between a bridging or "neighboring group" and an electron deficient center for to do otherwise would necessitate extensive rehybridization of one of the ring carbons with the consequent loss of considerable aromatic resonance energy [12] e.g.:



To test this concept and apply it to ferrocene derivatives these investigators prepared a series of α- and *p*-phenylene-substituted carbinyl chloride (A—C where X = methoxyl, thioethoxymethyl or ferrocenyl) and determined their solvolysis rates in 95% aqueous ethanol at 25°C. Defining a conjugative substituent param-



$$\text{G—C(CH}_3\text{)(H)—Cl} \xrightarrow[25^\circ\text{C}]{\text{EtOH/H}_2\text{O}} \text{G—C}^+\text{(CH}_3\text{)(Cl)} + \text{Cl}^-$$



eter, σ_α^+, and a transmission coefficient, τ_p *, for p-phenylene as:

$$\log k_A - \log k_B = \rho\sigma^+_{\alpha\text{-X}} = \tau_p \rho\sigma^+_{p\text{-X}} \tag{1}$$

or

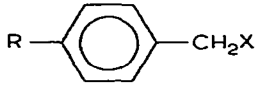
$$\tau_p = (\sigma^+_{\alpha\text{-X}}/\sigma^+_{p\text{-X}}) \tag{2}$$

where $\sigma_{p\text{-X}}$ is derived in the usual manner, viz.:

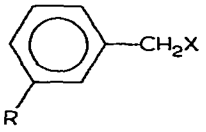
$$\log k_C - \log k_B = \rho\sigma^+_{p\text{-X}}, \tag{3}$$

they calculate that τ_p is ~2.0 for both methoxyl and ferrocenyl but is much larger in the case of thioethoxymethyl, a typical "neighboring group". A similar value of τ_p can be derived from the carbonyl stretching frequency of acetylferrocene [5e]. On this basis Traylor and Ware infer that similar modes of electron donation prevail with methoxyl and ferrocenyl and conclude that the electron donating effect of the latter is due to resonance (σ—π delocalization) rather than to a "neighboring group" interaction such as d-orbital bridging [5].

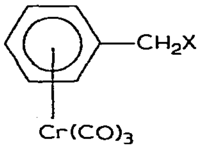
For some time now we have been interested in the solvolytic reactivity of β-(π-arylchromium tricarbonyl)alkyl derivatives and in this connection have suggested that a π-arylchromium tricarbonyl group may also provide some stabilization at cationic centers β to the ring [13]. In estimating the extent of such "homostabilization", we have routinely corrected our data for the rate-retarding inductive effect of the π-complexed tricarbonylchromium moiety by utilizing the p-nitrophenyl derivative as a model for π-phenylchromium tricarbonyl in the absence of participation **. The rigorous application of this procedure leads to computed solvolytic rate enhancements as large as 10^5 for some π-complexed β-phenylalkyl derivatives [13d].



(I) R = C_6H_5
(II) R = π-$(C_6H_5)Cr(CO)_3$
(III) R = p-$NO_2C_6H_4$
(VII) R = H
(VIII) R = CH_3
(IX) R = F
(X) R = Cl
(XI) R = CF_3
(XIV) R = OCH_3
(XV) R = NO_2



X = OTs , Cl
(IV) R = C_6H_5
(V) R = π-$(C_6H_5)Cr(CO)_3$
(VI) R = p-$NO_2C_6H_4$
(VII) R = H
(XII) R = Cl
(XIII) R = CF_3



(XVI)

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* This may better be thought of as an "insulation coefficient" since the more positive (τ_p-1) becomes, the smaller the electronic effect transmitted between the substituent X and the reaction site.

** This correction is based upon a suggestion of Nicholls and Whiting [14] who report that the pKa's of p-nitrophenyl- and π-chromium tricarbonyl complexed phenylacetic acids are similar viz. 5.02 and 5.01, respectively, in 50% ethanol at 25°C [13b].

In order to assess the extent of σ—π delocalization * in π-chromium tricarbonyl complexes and to check the validity of our previous corrections for inductive retardation we have attempted to determine accurate substituent parameters for the relevant groups under comparable solvolytic conditions. To this end we have prepared and measured the acetolytic reactivities of the biphenylcarbinyl tosylates I—VI.

Results

The *para*- and *meta*-substituted biphenylcarbinyl tosylates I—VI were prepared as described in the Experimental Section. Titrimetric acetolysis constants, activation parameters and "*b*" values [15] for added sodium acetate are recorded in Table 1 and 2.

TABLE 1

APPARENT FIRST ORDER ACETOLYSIS CONSTANTS AND ACTIVATION PARAMETERS OF *para*- AND *meta*-SUBSTITUTED BENZYL TOSYLATES [a]

Run	Compound	Temperature [b] (°C)	$10^6 k_t$(sec^{-1})	ΔH^*(kcal/mol)	ΔS^*(e.u.)
1,2	I-OTs	35.0	144 ± 1	19.4 [c]	—13.1 [c]
3	I-OTs	35.0	156 [d]		
4	I-OTs	35.0	170 [e]		
5	I-OTs	35.0	183 [f]		
6	I-OTs	35.0	81.8 [g]		
7,8	I-OTs	68.6	3635 ± 65		
9,10	II-OTs	35.0	60.4 ± 0.9	22.3 [h]	—5.6 [h]
11	II-OTs	35.0	50.2 [i]		
12	II-OTs	35.0	55.7 [j]		
13	II-OTs	35.0	77.0 [k]		
14	II-OTs	35.0	80.9 [l]		
15	II-OTs	35.0	67.5 [g]		
16,17	II-OTs	68.6	2400 ± 50		
18,19	III-OTs	35.0	6.68 ± 0.17	21.9 [m]	—11.3 [m]
20	III-OTs	68.5	291 [n]		
21	III-OTs	68.5	316 [k]		
22	III-OTs	68.5	341 [o]		
23	III-OTs	68.5	373 [p]		
24,25	III-OTs	68.6	249.5 ± 0.5		
26	III-OTs	68.6	302 [g]		
27,28	IV-OTs	68.5	190.5 ± 3.5	21.9 [q]	—11.7 [q]
29,30	IV-OTs	98.0	2960 ± 40		
31,32	V-OTs	69.9	46.75 ± 0.15		
33,34	VI-OTs	54.4	14.1 ± 0.1	21.4 [r]	—15.5 [r]
35,36	VI-OTs	69.6	63.7 ± 0.4		
37,38	VI-OTs	83.5	226 ± 5		

[a] Contains 0.0136—0.0250 *M* R-OTs and no added sodium acetate unless otherwise specified. [b] Controlled to ±0.03°. [c] Computed from runs 1, 2, 7, and 8. [d] Contains 0.0365 *M* sodium acetate. [e] Contains 0.0497 *M* sodium acetate. [f] Contains 0.0753 *M* sodium acetate. [g] Contains ~0.05 *M* sodium *p*-toluenesulfonate. [h] Computed from runs 9, 10, 16 and 17. [i] Contains 0.028 *M* sodium acetate. [j] Contains 0.038 *M* sodium acetate. [k] Contains 0.050 *M* sodium acetate. [l] Contains 0.087 *M* sodium acetate. [m] Computed from runs 18, 19, 24, and 25. [n] Contains 0.03589 *M* sodium acetate. [o] Contains 0.06363 *M* sodium acetate. [p] Contains 0.075 *M* sodium acetate. [q] Computed from runs 27—30. [r] Computed from runs 33—38.

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* Stabilization by resonance of a reactive site β to a π-complexed organometallic is termed σ—π homoconjugation.

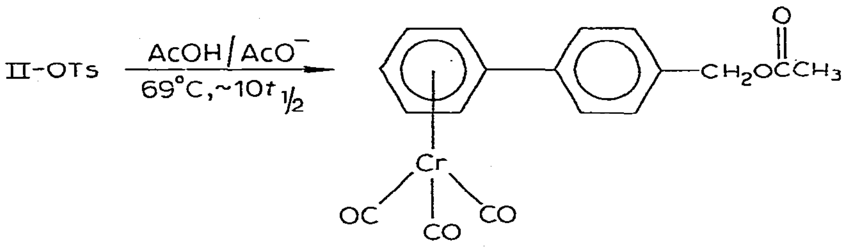
TABLE 2

DEPENDENCE OF APPARENT FIRST-ORDER ACETOLYSIS CONSTANTS OF *para*-SUBSTITUTED BENZYL TOSYLATES UPON ADDED SODIUM ACETATE

Compound	Temperature (°C)	$10^6 k_t^\circ$ [a] (sec^{-1})	b [b]
I-OTs	35.0	133	5.2 [c]
II-OTs	35.0	40	~13 [d]
III-OTs	68.5	212	10 [e]
VII-OTs	40.0		4.8 [f]

[a] Extrapolated value at zero acetate concentration. [b] Calculated from the relation $k_t = k_t^\circ(1 + b[\text{NaOAc}])$ [15]. [c] Calculated from runs 3—5; $(k_t^\circ)_{\text{extrapolated}} = 0.92(k_t^\circ)_{\text{measured}}$. [d] Calculated from runs 11—14; $(k_t^\circ)_{\text{extrapolated}} \approx 0.66(k_t^\circ)_{\text{measured}}$. [e] Calculated from runs 20—23; $(k_t^\circ)_{\text{extrapolated}} = 0.85(k_t^\circ)_{\text{measured}}$. [f] Ref. 16.

Each of the biphenylcarbinyl-type tosylates, I—VI, is presumed to produce the corresponding acetate under these conditions. This was demonstrated specifically in the case of p-(π-phenylchromium tricarbonyl)benzyl p-toluenesulfonate (II-OTs) e.g.:



In the manner of Streitwieser et al. [16] a plot of log k_t for acetolysis at 69°C vs. the conjugative substituent parameter, σ^+, of R [17] for tosylates, I, IV, VII and VIII—XIII (Table 3) defines two linear free energy relations, cf. Fig. 1. For the activating and mildly deactivating substituents p-CH_3, p-C_6H_5, p-F, H, m-C_6H_5 and p-Cl the weighted least square regression of log k on σ^+ [18] yields eq. 4, while for the more strongly deactivating substituents m-Cl, m-CF_3 and p-CF_3 a

$$\log k\,(\text{RC}_6\text{H}_4\text{CH}_2\text{OTs, HOAc, 69°C}) = -4.81\,\sigma^+ - 3.30 \qquad (4)$$

$$\log k\,(\text{RC}_6\text{H}_4\text{CH}_2\text{OTs, HOAc, 69°C}) = -2.68\,\sigma^+ - 3.63 \qquad (5)$$

similar treatment yields eq. 5. A similar treatment for acetolysis at 25°C (Table 3), Fig. 2 yields eq. 6 for p-OCH_3, p-CH_3, p-C_6H_5, p-F and H *, and eq. 7 for m-Cl, m-CF_3 and p-CF_3.

$$\log k\,(\text{RC}_6\text{H}_4\text{CH}_2\text{OTs, HOAc, 25°C}) = -6.07\,\sigma^+ - 5.55 \qquad (6)$$

$$\log k\,(\text{RC}_6\text{H}_4\text{CH}_2\text{OTs, HOAc, 25°C}) = -2.60\,\sigma^+ - 5.83 \qquad (7)$$

Since the acetolysis rates of both I- and IV-OTs are reasonably well correlated by the linear free energy relations (especially at 69°C) eq. 4—7 can be used to establish σ^+ values for the remaining biphenylcarbinyl-type derivatives II, III,

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* Nonweighted least square regression of log k_t on σ^+.

TABLE 3

SUMMARY OF RATE PARAMETERS FOR THE ACETOLYSIS OF BENZYL-TYPE TOSYLATES

Compound	Temperature (°C)	k(sec^{-1})	log k	ΔH^* (kcal/mole)	ΔS^* (e.u.)
I-OTs	25.0 [a]	4.79×10^{-5}	−4.320	19.4 [b]	−13.1 [b]
	69.0 [a]	3.77×10^{-3}	−2.424		
II-OTs	25.0 [a]	1.73×10^{-5}	−4.762	22.3	−5.6 [b]
	69.0 [a]	2.50×10^{-3}	−2.602		
III-OTs	25.0 [a]	1.96×10^{-6}	−5.708	21.9 [b]	−11.3 [b]
	69.0 [a]	2.60×10^{-4}	−3.585		
IV-OTs	25.0 [a]	1.50×10^{-6}	−5.824	21.9 [b]	−11.7 [b]
	69.0 [a]	2.00×10^{-4}	−3.699		
V-OTs	69.0 [b]	4.68×10^{-5}	−4.330		
VI-OTs	25.0 [a]	5.11×10^{-7}	−6.292	21.4 [b]	−15.5 [b]
	69.0 [a]	6.02×10^{-5}	−4.220		
VII-OTs	25.0	2.79×10^{-6}	−5.554	22.0 [c]	−10.3 [c]
	69.0 [d]	3.50×10^{-4}	−3.456		
VIII-OTs	25.0 [d]	1.66×10^{-4}	−3.780	20.3 [c]	−7.7 [c]
	69.0 [d]	1.58×10^{-2}	−1.801		
IX-OTs	25.0 [c]	7.12×10^{-6}	−5.148	21.55 [c]	−9.8
	69.0 [d]	8.73×10^{-4}	−3.059		
X-OTs	25.0	1.35×10^{-6}	−5.870	21.7 [c]	−12.4 [c]
	69.0 [d]	1.89×10^{-4}	−3.724		
XI-OTs	25.0 [d]	4.04×10^{-8}	−7.394	21.8 [c]	−19.2 [c]
	69.0 [d]	5.32×10^{-6}	−5.274		
XII-OTs	25.0 [c]	1.36×10^{-7}	−6.866	22.2 [c]	−15.4 [c]
	69.0 [d]	2.00×10^{-5}	−4.699		
XIII-OTs	25.0 [d]	6.31×10^{-8}	−7.200	24.4 [c]	−16.3 [c]
	69.0 [d]	9.48×10^{-6}	−5.023		
XIV-OTs	25.0 [e]	1.54×10^{-1}	−0.812		

[a] Computed from the activation parameters, see Table 1. [b] Our data, see Table 1. [c] Ref. 16. [d] Computed from the activation parameters of Streitwieser et al. [16]. [e] Estimated by Brown et al., cf. ref. 19.

V, and VI under conditions similar to those utilized in our earlier studies, cf. Table 6.

In order to compute σ_α^+ and τ_p for π-(C$_6$H$_5$)Cr(CO)$_3$ from solvolysis data, rate constants for a common π-benzylchromium tricarbonyl, XVI, and p-(π-phenylchromium tricarbonyl)benzyl derivative, II, under comparable conditions at a known ρ are required in addition to σ_p^+. Since we were unable to prepare and solvolyse XVI-OTs in acetic acid, it is necessary to compare the solvolysis rates of the corresponding chlorides, II- and XVI-Cl, in 80 vol % acetone/water at 25°C, the only condition for which the solvolytic rate of a π-benzylchromium tricarbonyl derivative (the chloride) is known [9]. From eq. 6, the acetolysis constant for p-nitrobenzyl tosylate, XV-OTs, at 25°C can be estimated: k(XV-OTs, HOAc, 25°C) $= 1.31 \times 10^{-8}$ sec^{-1} cf. Fig. 2. From the data of Tommila et al. [20] for the solvolysis of substituted benzyl chlorides in acetone/water mixtures, rate constants for the hydrolysis of p-methyl-, p-chloro-, and p-nitrobenzyl chloride (VIII-, X- and XV-Cl, respectively) in 80 vol % acetone/water at 25°C can be estimated, cf. Table 4. A plot of log k(RC$_6$H$_4$CH$_2$OTs, HOAc, 25°C) (Table 3) vs. log k(RC$_6$H$_4$CH$_2$Cl, 80 vol % acetone/water 25°C) (Table 4) for R = p-CH$_3$, p-Cl and p-NO$_2$ gives a reasonably good straight line, cf. Fig. 3, extending over the span of acetolytic reactivities represented by all the data in Table 3 except

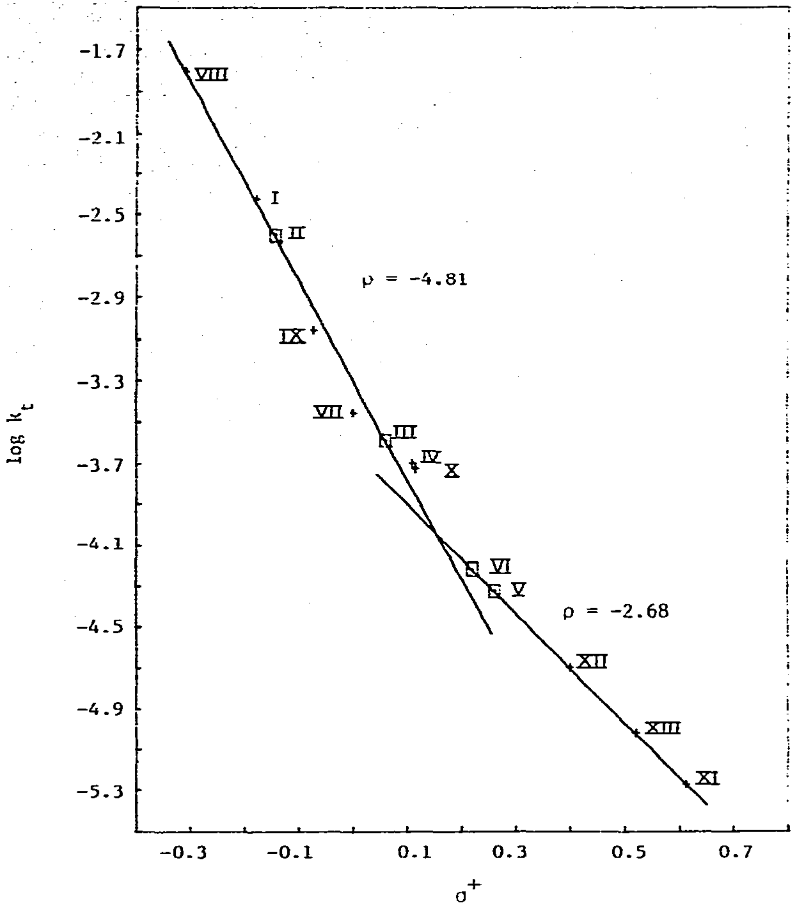

Fig. 1. $\rho\sigma^+$ correlation for acetolysis of substituted benzyl tosylates at 69°C (+) showing division into two lines and the newly determined σ^+ values (⊡).

that for XIV-OTs *. From the equation for this line:

$$\log k(\mathrm{RC_6H_4CH_2Cl},\ 80\ \mathrm{vol\ \%\ acetone/water},\ 25^\circ) =$$
$$0.355 \log(\mathrm{RC_6H_4CH_2OTs},\ \mathrm{HOAc},\ 25^\circ\mathrm{C}) - 6.25 \qquad (8)$$

the acetolysis data of Table 3, and the known [17] and derived σ^+ values (at 25°C for consistency, Table 6), the hydrolysis constants of the series of benzyl chlorides I—XV can be estimated, Table 4.

A Streitwieser plot (Fig. 4) of the estimated hydrolysis constants, Table 4, vs. σ^+ permits an estimation of the ρ value for activating groups, eq. 9,

$$\log k(\mathrm{RC_6H_4CH_2Cl},\ 80\ \mathrm{vol\ \%\ acetone/water},\ 25^\circ\mathrm{C}) = 2.19\,\sigma^+ - 8.24 \qquad (9)$$

under solvolytic conditions similar to those utilized by Pettit for the solvolysis

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* Such correlations in the case of benzyl derivatives have been observed previously. [21] We also find an excellent linear correlation between our acetolysis data at 25°C and the data of Olivier [22] on the hydrolysis of substituted benzyl chlorides (p-CH_3, H, p-Cl and m-Cl) in 50 vol % acetone-water at 25°C.

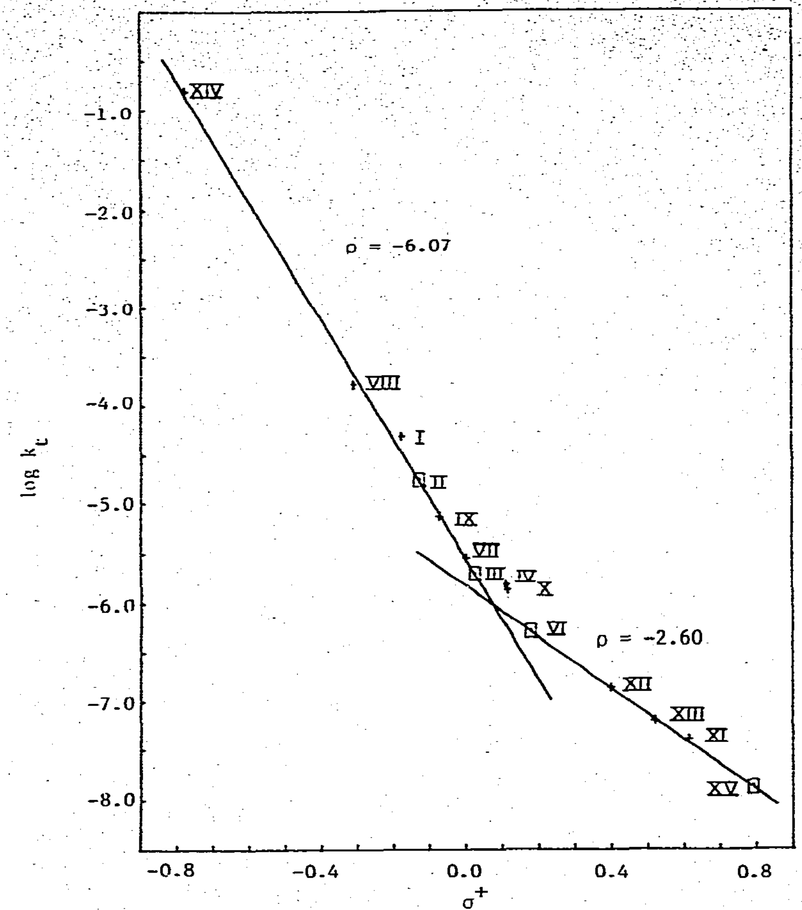

Fig. 2. $\rho\sigma^+$ correlation for acetolysis of substituted benzyl tosylates at 25°C (+) showing division into two lines and the newly determined σ^+ or log k_t values (▣).

of chromium tricarbonyl-complexed benzyl chloride (XVI) [9], Table 4. From eq. 9, in the manner of Traylor and Ware [5e], σ_α^+ for π-$(C_6H_5)Cr(CO)_3$ can be estimated, e.g.

$$\begin{aligned}\sigma_\alpha^+[\pi\text{-}(C_6H_5)Cr(CO)_3] &= (\log k(\mathrm{XVI}) + 8.24)/\rho \\ &= (-3.66 + 8.24)/(-2.19) = -2.09\end{aligned}$$

and

$$r_p = \frac{\sigma_\alpha^+}{\sigma_p^+} = \frac{-2.09}{-0.130} = 16$$

When calculated from the data of Gubin et al., [24] *, Table V, and the linear free energy relation of Okamoto and Brown [25b] for the hydrolysis of substituted cumyl chlorides, viz.:

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* We thank Dr. Gubin for a helpful discussion and a preprint of his paper prior to its publication [24b].

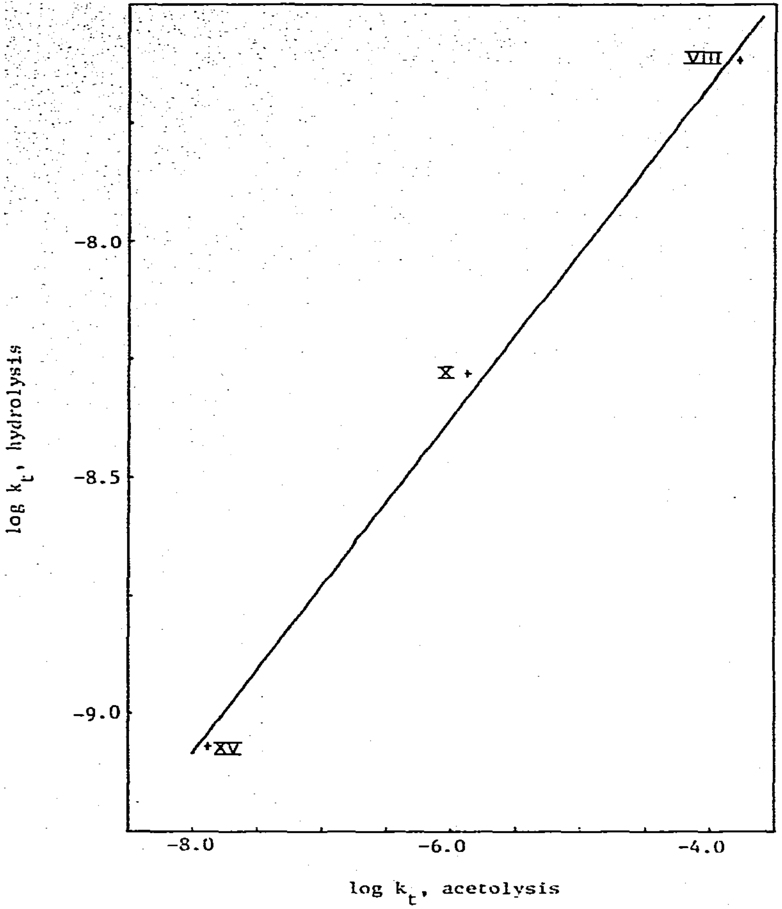
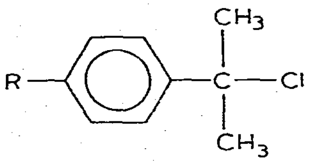
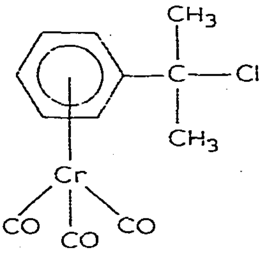


Fig. 3. Log k_t for acetolysis of substituted benzyl tosylates at 25°C vs. log k_t for hydrolysis of substituted benzyl chlorides in 80 vol % acetone/water at 25°C, cf. eq. 8.



(XVII) R = C_6H_5
(XVIII) R = π-$(C_6H_5)Cr(CO)_3$
(XIX) R = H



(XX)

$$\log k(RC_6H_4C(CH_3)_2Cl,\ 90\ \text{vol}\ \%\ \text{acetone/water},\ 25^\circ C) = -4.54\ \sigma^+ - 3.907 \quad (10)$$

$\sigma_\alpha^+[\pi\text{-}(C_6H_5)Cr(CO)_3] = -0.322$, $\sigma_p^+ = -0.09$ and $\tau_p = 3.6$.

The derived conjugative substituent parameters for π-$(C_6H_5)Cr(CO)_3$ and ferrocenyl are compared in Table 6 with those of nitro and methoxyl.

TABLE 4

SUMMARY OF ESTIMATED RATE CONSTANTS FOR THE SOLVOLYSIS OF BENZYL-TYPE CHLORIDES IN 80 Vol % ACETONE/WATER AT 25°C [a]

Compound	Substituent R	σ_R^+	k (sec^{-1})	log k
I-Cl	p-C_6H_5	−0.179 [b]	1.65×10^{-8}	−7.784
II-Cl	p-[π-(C_6H_5)Cr(CO)$_3$]	−0.130 [c]	1.15×10^{-8}	−7.941
III-Cl	p-(p'-$O_2NC_6N_4$)	+0.026 [c]	5.29×10^{-9}	−8.276
IV-Cl	m-C_6H_5	+0.109 [b]	4.81×10^{-9}	−8.318
VI-Cl	m-(p'-$O_2NC_6H_4$)	+0.178 [c]	3.28×10^{-9}	−8.484
VII-Cl	H	0.0 [b]	6.00×10^{-9}	−8.222
VIII-Cl	p-CH_3	−0.311 [b]	2.42×10^{-8} [d,e]	−7.617
IX-Cl	p-F	−0.073 [b]	8.36×10^{-9}	−8.078
X-Cl	p-Cl	+0.114 [b]	5.26×10^{-9} [d,f]	−8.279
XI-Cl	p-CF_3	+0.612 [b]	1.33×10^{-9}	−8.875
XII-Cl	m-Cl	+0.399 [b]	2.05×10^{-9}	−8.687
XIII-Cl	m-CF_3	+0.520 [b]	1.56×10^{-9}	−8.806
XIV-Cl	p-OCH_3	−0.778	2.90×10^{-7}	−6.538
XV-Cl	p-NO_2	+0.790 [b]	8.45×10^{-10} [d,g]	−9.073
XVI-Cl	π-Cr(CO)$_3$		2.2×10^{-4} [h]	−3.658

[a] Calculated from eq. 8 and the data of Table 3. [b] Ref. 17. [c] Table 6. [d] Estimated from the data of ref. 20 using the Winstein—Grunwald correlation, $\log k = mY + \log k_0$, ref. 23. This point was utilized to derive eq. 8. [e] $m = 0.842$, $\log k_0 = -7.050$. [f] $m = 0.646$, $\log k_0 = -7.844$. [g] $m = 0.615$, $\log k_0 = -8.659$. [h] Ref. 9.

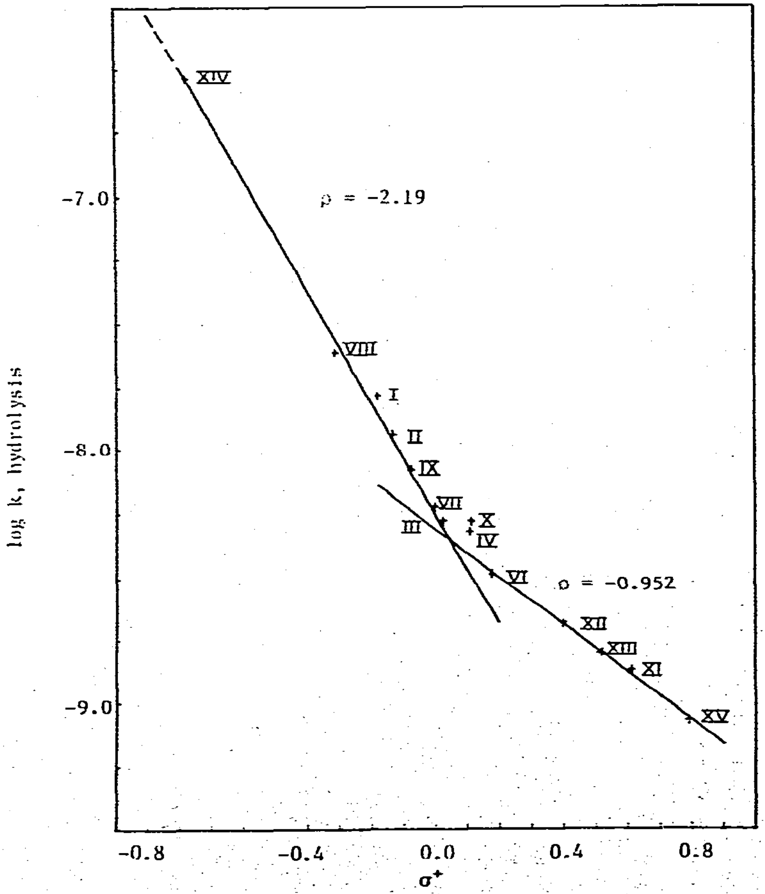


Fig. 4. Derived $\rho\sigma^+$ correlation for hydrolysis of substituted benzyl chlorides in 80 vol % acetone/water at 25°C showing predicted division into two lines.

TABLE 5

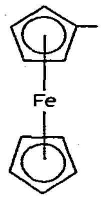
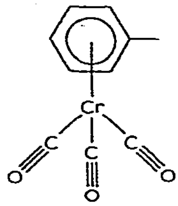
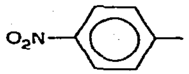
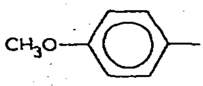
SUMMARY OF RATE PARAMETERS FOR THE HYDROLYSIS OF CUMYL-TYPE CHLORIDES IN 90 vol % ACETONE/WATER AT 25°C

Compound	10^4k (sec^{-1})	ΔH^* (kcal/mole)	ΔS^* (e.u.)
XVII	8.33	18.0[a]	−12.2[a]
XVIII	3.34	10	−39
XIX	1.3	18.8[b]	−12.5[b]
XX	36.0	6	−50

[a] Ref. 25c. [b] Ref. 25a.

TABLE 6

CONJUGATIVE SUBSTITUENT PARAMETERS FOR ORGANOMETALLIC π-COMPLEXES FROM KINETIC AND THERMODYNAMIC DATA

	σ_m^+	σ_p^+	σ_α^+	τ_p
	0[a]	−0.7[a]	−1.4[a] −1.55[b] −2.45[c] −1.7[d] −1.3[e]	2.0
	+0.262[f]	−0.144[f] −0.13[g] −0.09[h]	−2.1[g] −0.32[h] −0.82[c,i] −0.75[d,j]	16[g] 3.6[h]
	0.221[f] 0.178[g]	0.060[f] 0.026[g]		
	0.047[a]	−0.778	~−1.4[a]	~2[a]

[a] From the solvolysis of α-substituted ethyl chlorides in 95 vol % ethanol/water at 25°C [5e]. [b] From the solvolysis of α-substituted ethyl acetates; unpublished work of M.L. Gross quoted in ref. 27. [c] From the pK_R^+ of α-ferrocenylbenzyl cation (0.1) [27] and diphenylmethyl cation (−13.4) [28]*, in sulfuric acid/ethanol/water at 25°C assuming a ρ of −5.5, [29]. [d] From the pK_R^+ of ferrocenylmethyl cation (−1.28) [27] an estimated pK_R^+ for benzyl cation of −20 and an estimated ρ of −11 [28]. [e] From the basicities of substituted methyl ketones [27]. [f] From the acetolysis of substituted benzyl tosylates at 69°C, see Fig. 1. [g] From the acetolysis of substituted benzyl tosylates at 25°C, see Fig. 2. [h] From the hydrolysis of substituted cumyl chlorides in 90 vol % acetone/water at 25°C (ρ −4.54), cf. Table 5 and ref. 24. [i] From the pK_R^+ of α-[π-PhCr(CO)$_3$]benzyl cation (−8.9) [28]. [j] From the pK_R^+ of π-benzylchromium tricarbonyl cation (−11.8) [28].

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* We thank Drs. Wells and Trahanovsky for a copy of this dissertation prior to publication [28].

Discussion

σ—π Delocalization by π-phenylchromium tricarbonyl. π-Phenylchromium tricarbonyl is inductively much more electron withdrawing than ferrocenyl. This fact is clearly revealed by its σ_m^+ value of +0.26 compared to ferrocenyl's σ_m^+ of ~0.0 (Table 6). It is noteworthy that our solvolytically derived value of σ_m^+ for π-phenylchromium tricarbonyl agrees well with the inductive parameters determined by Gubin et al. from the ^{19}F NMR of *m*-(π-phenylchromium tricarbonyl)fluorobenzene (σ_i = +0.21) [30] and from the dissociation constant of (π-phenylchromium tricarbonyl)acetic acid (σ_p^0 = +0.26) [26]. The σ_m^+ for *p*-nitrophenyl is only slightly smaller, +0.22, than that of π-phenylchromium tricarbonyl, thus validating our previous use of *p*-nitro derivatives as solvolytic models for the rate-retarding inductive effect of π-tricarbonylchromium [14].

Although direct comparison is difficult because comparable data are not available in the two systems, the estimated σ_α^+ values included in Table 6 suggest that π-phenylchromium tricarbonyl is a substantially poorer electron donor than ferrocenyl. The best single indication of this is probably the fact that α-ferrocenylbenzyl cation is about 9 p*K* units more stable than α-(π-phenylchromium tricarbonyl)benzyl cation [27,28]. While σ_α^+ for the solvolysis of π-complexed benzyl chloride (XVI), a primary system, is apparently * more negative (—2.1) than σ_α^+ for the solvolysis of either of the secondary derivatives, α-ferrocenylethyl chloride (—1.4) or acetate (—1.55), the significance of this comparison is obscured by the fact that σ_α^+ for chromium tricarbonyl complexed cumyl chloride, a tertiary derivative, is much less negative (—0.32) [24]. Since σ_α^+ for a particular electron-donating substituent is expected to become less negative as electron demand is decreased at the electrophilic center in the order primary > secondary > tertiary, a primary α-ferrocenyl derivative would presumably exhibit a σ_α^+ value of less than —2. It can, of course, be quite misleading to judge the relative electronic effect of two substituents such as ferrocenyl and π-phenylchromium tricarbonyl on the basis of relative reaction rates alone unless the conditions are comparable and ρ is known.

Even though π-phenylchromium tricarbonyl is a poorer electron donor it is comparable to α-ferrocenyl as a conjugative substituent. If we accept that the inductive withdrawal of π-tricarbonylchromium is approximately equal to that of *p*-nitro (σ_p +0.778) [14,17] then the overall conjugative effect of α-(π-phenylchromium tricarbonyl) $\sigma_{\alpha c}^+$, must approximate σ_α^+ —0.8, a value which in each of the cases listed in Table 6 is comparable to σ_α^+ of ferrocenyl for which an electronegativity correction would be much less important **. A com-

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* Although nearly ideal from the experimental point of view, the acetolysis of benzyl-type tosylates is certainly not the best system from a mechanistic viewpoint with which to access the conjugative ability of a substituent such as π-phenylchromium tricarbonyl. In the first place it is highly likely that nucleophilic solvent participation plays a significant part in the overall reaction so that the process may be far from "limiting". Secondly, it is not clear that highly activated benzyl tosylates such as *p*-methoxyl, *p*-ferrocenyl or *p*-[π-phenylchromium tricarbonyl] would, as we and others [19] have assumed, fall on the same correlation line, i.e., have the same ρ-value, as moderately activated ones such as *p*-methyl, *m*-methyl and *p*-fluoro [16]. The rate constant for the acetolysis of *p*-methoxybenzyl tosylate at 25°C (Table 3) is estimated from those of the less reactive *m*-chloro and *m*-chloro-*p*-methoxy derivatives by assuming a similar ρ for its solvolysis [19].

** For ferrocenyl, σ_m^+ 0.0. The pK_a of ferrocenecarboxylic acid in 38 vol % ethanol at 20°C is 5.72 ± 0.01 [31], while that of benzoic acid in 41 vol % ethanol is 5.16 [32].

parable correction in the case of σ_p^+ yields $\sigma_{pc}^+ \approx \sigma_p^+ - \sigma_m^+ = -0.144 - 0.262 \approx -0.4$ compared to σ_{pc}^+ (ferrocenyl) of -0.7.

The electronic effect of π-phenylchromium tricarbonyl appears to be attenuated more effectively by an interposed *p*-phenylene than is that of ferrocenyl. This is clearly indicated by the larger values of τ_p, 16 and 3.6, observed in the case of π-phenylchromium tricarbonyl, Table 6. A more meaningful comparison, however, would probably be that of a "conjugative" transmission coefficient, τ_{pc}, defined as:

$$\tau_{pc} = \sigma_{\alpha c}^+ / \sigma_{pc}^+$$

since it is the effect of *p*-phenylene upon the conjugative electron-donating ability of ferrocenyl and π-phenylchromium tricarbonyl with which we are most directly concerned. For the solvolysis of benzyl chlorides in 80% acetone at 25°C $\tau_{pc} = (\sigma_\alpha^+ - 0.8)/(\sigma_p^+ - 0.26) = 7.1$ and for the solvolysis of cumyl chlorides in 90% acetone at 25°C $\tau_{pc} = (-0.32 - 0.8)/(-0.09 - 0.26) = 3.2$. Since $\tau_{pc} \approx \tau_p$ in the case of ferrocenyl these values can be compared directly with τ_p (ferrocenyl) = 2.0 for the solvolysis of α-arylethyl chloride in 95% ethanol at 25°C [5e]. If the "Traylor τ test" has validity, these results suggest that, in apparent contrast to ferrocenyl (and methoxyl), α-(π-phenylchromium tricarbonyl) may owe some of its ability to stabilize adjacent electron-deficient centers to an effect other than σ—π delocalization. We suspect direct *d*-orbital bridging [13]. The presence of such *d*-orbital bridging in α-(π-phenylchromium tricarbonyl) derivatives would appear to be a necessary but not sufficient condition for its occurrence in the reactions of chromium tricarbonyl-complexed β-arylethyl compounds.

Experimental *

p-Phenylbenzyl p-toluenesulfonate (I-OTs). I-OTs was prepared according to the procedure of Hammond and Reeder [33] from *p*-phenylbenzyl alcohol (K and K Laboratories, Inc., m.p. 99—101°C lit. [33] 100.5—101.0°). Recrystallization of the crude product from an ether/pentane mixture gave colorless needles, m.p. 114—115°C (lit. [33] 114°C, dec.) in 38% yield. Infrared analysis (ν, cm^{-1}) showed [34] (KBr): 3030 (C—H phenyl); 1605, 1500, 1465 (phenyl nucleus); 1370, 1188, 1173 ($R—SO_2—OR'$); 1095 (O—R'); 863, 820 (*p*-phenylene?); 790, 760, and 693 (phenyl?); NMR [35] (CD_3COCD_3): δ(ppm) 7.9—7.1, complex multiplet (the superposed resonances of the phenyl and the two *p*-phenylene rings, (e.g., $C_6H_5—C_6H_4—$ and $—C_6H_4—$); 5.10, singlet ($—C_6H_4—CH_2—O—$); 2.40, singlet ($—C_6H_4CH_3$). Anal. Found: C, 70.88; H, 5.48; O, 14.02. $C_{20}H_{18}O_3S$ calcd.: C, 70.98; H, 5.36; O, 14.18; S, 9.47%.

p-Phenylbenzyl acetate. A mixture of 0.25 g (1.4 mmol) *p*-phenylbenzyl

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[*] Melting points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches 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 using tetramethylsilane as an external standard. Thin layer chromatography was carried out on silica gel (E. Merck, P_{254}, Brinkmann Instruments, Inc.) using a 1 : 1 ether/pentane for development and iodine vapor and/or ultraviolet light for visualization.

alcohol (K and K Laboratories, Inc., m.p. 99—101°C, lit. [33] 100.5—101.0°C), 0.3 ml acetic anhydride and 1 ml dry pyridine was allowed to stand overnight at room temperature, poured into cold water (5 ml) and extracted with ether. The ethereal solution was washed successively with cold 10% aqueous bicarbonate and water then dried over anhydrous magnesium sulfate. The filtrate was concentrated by slow evaporation and pentane was added. When the solution was cooled to −20°C, 0.20 g (65%) of white crystals precipitated, m.p. 32—33°C. Infrared analysis (ν, cm^{-1}) showed [34] ($CHCl_3$): 3030 (C—H aromatic); 2960, 2870, 1460, 1380 (—CH_3); 1745 (C=O ester); 1610, 1500 (phenyl nucleus); 1240, 1030 (CH_3COO—) 840 (*p*-phenylene ?); and 703 (phenyl ?); NMR [35] ($CDCl_3$): δ(ppm) 7.7—7.1, complex multiplet (C_6H_5—C_6H_4—); 5.10, singlet (—C_6H_4—CH_2—O—); 2.08, singlet (—$OCOCH_3$).

Methyl p-(π-phenylchromium tricarbonyl)benzoate. A mixture of 4.24 g (20.0 mmol) methyl *p*-phenylbenzoate (m.p. 117—118°C, lit. [36] 116.5°C), 4.4 g (20 mmol) chromium hexacarbonyl, 6 ml anhydrous diglyme, 10 ml anhydrous glyme and 40 ml isooctane was heated under reflux (160—165°C) in a Stohmeier apparatus [37] for 26 h. The cooled reaction mixture was taken up in ether, filtered through charcoal and the golden-yellow filtrate was washed thoroughly with water. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to deposit an orange solid, which upon recrystallization from acetone/ether gave 1.8 g (26%) of orange crystals, m.p. 169—171°C (lit. [28b] 163—166.5°C). IR analysis (ν, cm^{-1}) showed [34] ($CHCl_3$): 2940, 2830 (C—H in OCH_3); 1980, 1900 (C≡O); 1728 (C=O ester); 1620, 1450 (phenyl nucleus); 1420, 1380 (—CH_3?); 1285, 1118 (C—O—C benzoate); 860, 840 (*p*-phenylene?); 705 (phenyl?); UV (C_2H_5OH): 253 (ϵ 18,580) and 333 nm (ϵ 6,960); NMR [35] ($CDCl_3$): δ(ppm) 8.15, 8.03, 7.62, 7.49, broad symmetric quartet, $J_{AB} = J_{A'B'} \approx 8$ Hz (—$C_6\underset{\sim}{H}^A\underset{\sim}{H}^{A'}\underset{\sim}{H}^B\underset{\sim}{H}^{B'}$—)*; 5.90—5.35(br) complex multiplet [$(CO)_3CrC_6\underset{\sim}{H}_5$—]; 3.97, singlet (—$COOC\underset{\sim}{H}_3$).

p-(π-Phenylchromium tricarbonyl)benzyl alcohol. To a slurry of 0.24 g (6.3 mmol) of lithium aluminium hydride in 15 ml of absolute ether at −60°C was added under dry, oxygen-free nitrogen a suspension of 1.6 g (4.6 mmol) of methyl *p*-(π-phenylchromium tricarbonyl)benzoate in 100 ml of ether. The temperature of the reaction mixture was allowed to rise to 15°C, 10 ml of ethanol was added slowly and the entire mixture was poured into cold, dilute sulfuric acid. The ethereal extract was washed successively with water, dilute, aqueous sodium bicarbonate and water then dried over anhydrous magnesium sulfate. Concentration to ~20 ml, addition of pentane and cooling to 0°C precipitated 1.2 g (81%) of yellow crystals, m.p. 95—96°C (lit. [28b] 95—96°C). IR analysis (ν, cm^{-1}) showed [34] ($CHCl_3$): 3595, 3400—3300 (O—H); 3070, 3020 (C—H aromatic); 1975, 1900 (C≡O); 1620, 1520, 1465 (phenyl nucleus); 1220, 1010 (C—O); 850, 835, 810 (*p*-phenylene?); 705 (phenyl?); NMR [28b, 35] (CD_3COCD_3): δ(ppm) 7.6—7.2, perturbed quartet $J_{AB} = J_{A'B'} \approx 8$ Hz (—$C_6\underset{\sim}{H}^A\underset{\sim}{H}^{A'}\underset{\sim}{H}^B\underset{\sim}{H}^{B'}$—); 6.1—5.5, complex multiplet [$(CO)_3CrC_6\underset{\sim}{H}_5$—]; 4.62, singlet (—$C\underset{\sim}{H}_2$—O—); 4.2—4.0(br) (—OH?).

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* This is a fairly typical example of a *p*-disubstituted aromatic ring whose normally complex AA′BB′ spectrum resembles that of an AB quartet because $|J_{AB}| = |J_{A'B'}| >> |J_{AA'}|, |J_{BB'}|$ and $|J_{AB'}| = |J_{A'B}|$ [38].

p-(π-Phenylchromium tricarbonyl)benzyl p-toluenesulfonate (II-OTs). A mixture of 0.80 g (2.5 mmol) of *p*-(π-phenylchromium tricarbonyl)benzyl alcohol in 10 ml of diglyme, 0.68 g (3.5 mmol) *p*-toluenesulfonyl chloride and 1.25 ml of 40% aqueous sodium hydroxide was stirred under oxygen-free nitrogen at 18°C for 15—16 h. The reaction mixture was poured into an ice/water mixture and the product was extracted into ether. The ethereal solution was washed with water and dried over anhydrous magnesium sulfate. Pentane was added and yellow crystals, 0.45 g (38%), m.p. 115—116°C, dec. precipitated when the solution was cooled. IR analysis (ν, cm^{-1}) showed [34] (KBr): 3080 (C—H aromatic); 2960 ($—CH_3$); 2980, 2880 (C≡O); 1610, 1510, 1465 (phenyl nucleus); 1370, 1190, 1180 ($R—SO_2—OR'$); 1093 (O—R′); 863, 820, 804 (*p*-phenylene?); 790 and 690 (phenyl?); UV (C_2H_5OH): 247 (ϵ 21,000) and 326 nm (ϵ 7,690); NMR [35] * (CD_3COCD_3): δ(ppm) 7.9—7.0, complex multiplet (the superimposed AA′BB′ resonance of two *p*-phenylenes, e.g., $—C_6H_4—$ and $C_6H_4—$); 6.05—5.35, complex multiplet [$(CO)_3CrC_6H_5—$]; 5.10, singlet ($—C_6H_4—C\underset{\sim}{H}_2—O—$); 2.40, singlet ($—C_6H_4—C\underset{\sim}{H}_3$). Anal. Found: C, 58.34; H, 3.96; O, 20.12; S, 6.64. $C_{23}H_{18}CrO_6S$ calcd.: C, 58.22; H, 3.82; Cr, 10.96; O, 20.23; S, 3.82%.

p-(π-Phenylchromium tricarbonyl)benzyl acetate. A mixture of 0.40 g (1.2 mmol) of *p*-(π-phenylchromium tricarbonyl)benzyl alcohol, 0.4 ml of acetic anhydride and 2 ml of dry pyridine was allowed to stand overnight at room temperature under dry, oxygen-free nitrogen. The reaction mixture was worked up in the manner described previously for the noncomplexed derivative, vide supra, to yield 0.25 g (58%) of yellow crystals, m.p. 90—92°C. Infrared analysis (ν, cm^{-1}) revealed [34] ($CHCl_3$): 3060, 3015 (C—H aromatic); 1980, 1910 (C≡O); 1745 (C=O ester); 1620, 1520, 1465 (phenyl nucleus); 1240, 1225 (C—O acetate); 870, 855, 845, 820 and 810 (*p*-phenylene?); UV (C_2H_5OH): 240 (ϵ 27,960) and 328 nm (ϵ 12,000); NMR [35] (CD_3COCD_3): δ(ppm) 8.0—7.2, complex multiplet, $J_{AB} = J_{A'B'} \approx 8$ Hz ($—C_6\underset{\sim}{H}^A\underset{\sim}{H}^{A'}\underset{\sim}{H}^B\underset{\sim}{H}^{B'}—$); 6.1—5.5, complex multiplet, [$(CO)_3CrC_6\underset{\sim}{H}_5—$]; 5.10, singlet ($—C_6H_4—C\underset{\sim}{H}_2—O—$); 2.07, singlet ($—OCOC\underset{\sim}{H}_3$). Anal. Found: C, 59.49; H, 3.82; O, 22.17. $C_{18}H_{14}CrO_5$ calcd.: C, 59.67; H, 3.90; Cr, 14.35; O, 22.08%.

Methyl 4′-nitro-4-biphenylcarboxylate. To 10.6 g (0.0499 mol) of methyl *p*-phenylbenzoate (m.p. 117—118°C, lit. [36] 116.5°C) dissolved in 120 ml of acetic anhydride was added 15 ml of concentrated nitric acid. The solution was stirred overnight at room temperature, then poured into an ice/water mixture and extracted with chloroform. The organic layer was washed successively with dilute, aqueous sodium bicarbonate and water then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure and recrystallization from a chloroform/pentane mixture afforded 6.0 g (47%) of yellow crystals, m.p. 189—190°C. Infrared analysis (ν, cm^{-1}) [34] ($CHCl_3$) revealed: 3095; 3040 (C—H aromatic); 2970, 2865 ($—CH_3$); 1960, 1820, 863, 858, 848, 832 (*p*-phenylene?); 1750 (benzoate C=O); 1620, 1460 (phenyl nucleus); 1550, 1375 ($—NO_2$); 1285, 1192, 1178, 1112 ($—COO—CH_3$); 695 (phenyl?); NMR [35] (CCl_4): δ(ppm) 8.1—7.2, approximately symmetric sextet (resulting apparently from the two overlapping AA′BB′ resonances of the two chemically nonequiv-

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* Using acetone-d_5 as an internal standard, $\delta(CHD_2)$ 2.02 relative to tetramethylsilane.

alent *p*-phenylene rings, e.g. $O_2N{-}C_6H^AH^{A'}H^BH^{B'}{-}C_6H^AH^{A'}H^BH^{B'}{-}$) [35], $\sim$3.66, singlet ($-COOCH_3$). Anal. Found: C, 65.25; H, 4.32; N, 5.51. $C_{14}H_{11}NO_4$ calcd.: C, 65.36; H, 4.31; N, 5.45; 0, 24.88%.

4′-Nitro-4-biphenylcarbinol. To 2.58 g (0.0100 mol) of methyl 4′-nitro-4-biphenylcarboxylate in 20 ml of 1,4-dioxane was added 1.1 g (0.050 mol of lithium borohydride and the mixture was stirred overnight at room temperature. Ethanol (15 ml) was added to the cooled reaction mixture and the resulting solution was poured into 50 ml of cold, dilute sulfuric acid. The cold aqueous solution was extracted with several portions of ether which were combined, washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue, when recrystallized from aqueous ethanol, gave 1.85 g (80.7%) of yellow crystals, m.p. 165—167°C. Infrared analysis [34] (KBr) showed: 3500 ($-O-H$); $\sim$3060, $\sim$3020 ($-C-H$ aromatic); 2940, $\sim$2870 ($-CH_2-$); 1710 ($-COOH$ dimer); 1600, 1435 (phenyl nucleus); 1510, 1330 ($-NO_2$); 1260, 1100 ($-C-OH$); 857, 842, $\sim$825 (*p*-phenylene ?); 746 (phenyl ?); NMR [35] ($CDCl_3$): δ(ppm) 8.4—7.3, complex multiplet ($O_2NC_6\underset{\sim}{H}_4{-}C_6\underset{\sim}{H}_4{-}$); 4.75, singlet ($-O\underset{\sim}{H}$); 3.90, singlet ($-C_6H_4{-}C\underset{\sim}{H}_2O{-}$). This material, which is obviously contaminated with a small amount of the carboxylic acid *, cf. infrared spectrum, was used for the preparation of the tosylate without further purification.

4′-Nitro-4-biphenylcarbinyl p-toluenesulfonate (III-OTs). A sample of 1.2 g (5.2 mmol) of 4′-nitro-4-biphenylcarbinol (m.p. 165—167°C, vide supra) was converted to the tosylate in the manner described previously, cf. *p*-(π-phenyl chromium tricarbonyl)benzyl *p*-toluenesulfonate (II). Recrystallization of the crude product from chloroform gave 1.2 g (60%) of light-yellow crystals, m.p. 90—92°C (dec.). Infrared analysis (ν, cm^{-1}) showed [34] ($CHCl_3$): 3020 ($C-H$ aromatic); 2950, 2870 ($-CH_3$); 2925, 2850 ($-CH_2-$); 1935, 1810, 870, 853, 818 (*p*-phenylene ?); 1615, 1450 (phenyl nucleus ?); 1535, 1360 (NO_2); 1375; 1185, 1172 ($R-SO_2-OR'$); 1093 ($O-R'$); 696 (phenyl?); NMR [35] ($CDCl_3$): δ(ppm) 8.4—7.1, complex multiplet (the superposed resonances of the three *p*-phenylene rings, e.g. $O_2N{-}C_6H_4{-}C_6H_4{-}$ and $-C_6H_4-$); 5.08, singlet ($-C_6H_4{-}CH_2{-}O{-}$); 2.42, singlet ($-C_6H_4{-}CH_3$). Anal. Found: C, 62.57; H, 4.34; N, 3.75; S, 8.28. $C_{20}H_{17}NO_5S$ calcd.: C, 62.65; H, 4.47; N, 3.65; O, 20.87; S, 8.36%.

m-Phenylbenzyl p-toluenesulfonate (IV-OTs). IV-OTs was prepared from *m*-phenylbenzyl alcohol (m.p. 50—51°C, lit. [33] 51.2—51.5°C) according to the procedure of Hammond and Reeder [33]. Recrystallization of the crude product from an ether/pentane mixture gave colorless needles, m.p. 77.5—78.5°C (lit. [33] 76—78° dec.) in 44% yield. Infrared analysis (ν, cm^{-1}) showed [34] ($CHCl_3$): 3055, $\sim$3025 ($C-H$ aromatic); 2925, 2870 ($C-H$ aliphatic); 1615, 1505, 1470 (phenyl nucleus); 1385, 1188, 1173 ($R-SO_2-OR'$); 1097 ($O-R'$); 840 (isolated H in *m*-phenylene ?); 818 (three adjacent H's in *m*-phenylene ?); 702 (phenyl ?); NMR ($CDCl_3$): δ(ppm) 7.73—6.9, complex multiplet (the superposed resonances of the phenyl, the asymmetrically substituted *m*-phenylene and the *p*-phenylene rings, e.g. $C_6\underset{\sim}{H}_5{-}C_6\underset{\sim}{H}_4{-}$ and $-C_6\underset{\sim}{H}_4-$); 5.07, singlet ($-C_6H_4{-}C\underset{\sim}{H}_2{-}O{-}$); 2.37, singlet ($-C_6H_4{-}C\underset{\sim}{H}_3$). Anal. Found: C, 71.03; H, 5.54;

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* We presume this contaminant was formed by hydrolysis of some unreduced ester during the acid work up of the borohydride reduction mixture.

O, 13.90. $C_{20}H_{18}O_3S$ calcd.: C, 70.98; H, 5.36; O, 14.18; S, 9.47%.

Methyl m-phenylbenzoate. This compound was prepared by esterification of *m*-phenylbenzoic acid [33] m.p. 165—166°C (lit. [33] 166.5—166.9°C) with excess ethereal diazomethane [39]. Recrystallization of the product from aqueous methanol gave white needles, m.p. 49—50°C in 80% overall yield. Spectral analysis confirmed the structure, viz., IR [34] (ν, cm^{-1}) ($CHCl_3$): 3050, 3020 (C—H aromatic); 2945, 2840 ($-CH_3$); 1730 (C=O benzoate); 1600, 1495 (phenyl nucleus); 1460, 1450 ($-CH_3$?); 1308, 1260, 1248 ($ArCOOCH_3$); 1170, 1113 (*m*-phenylene ?); 848 (isolated H in *m*-phenylene ?); 822 (*m*-phenylene ?); 702 (phenyl?); NMR [35] ($CDCl_3$): 8.3—7.1, complex multiplet (the overlapping resonances of the phenyl and the ABCD pattern of the asymmetrically substituted *m*-phenylene, e.g. $C_6H_5-C_6H_4-$); 3.87, singlet ($-COOCH_3$). Anal. Found: C, 79.34, H, 5.78% *. $C_{14}H_{12}O_2$ calcd.: C, 79.22; H, 5.70; O, 15.08.

Methyl m-(π-phenylchromium tricarbonyl)benzoate. This compound was prepared from methyl *m*-phenylbenzoate in the manner described previously for the *para* isomer, vide supra. The crude material when recrystallized from an acetone/ether mixture produced yellow crystals, m.p. 110—112°C in 25% overall yield. Infrared analysis [34] (ν, cm^{-1}) revealed ($CHCl_3$): 1980, 1905 (C≡O); 1735 (C=O benzoate); ~1600, 1490 (phenyl nucleus); 1460 ($-CH_3$?); 1308, 1248 ($ArCOOCH_3$); 1113 (*m*-phenylene ?); NMR [35] (CD_3COCD_3): δ(ppm) 8.2—7.3, asymmetric septet ($-C_6\underline{H}^A\underline{H}^B\underline{H}^C\underline{H}^D-$); 6.2—5.5, complex multiplet [$(CO)_3CrC_6\underline{H}_5-$]; 3.88, singlet ($-OCOC\underline{H}_3$). Anal. Found: C, 58.78; H, 3.56; O, 22.86. $C_{17}H_{12}CrO_5$ calcd.: C, 58.63; H, 3.47; Cr, 14.93; O, 22.97%.

m-(π-Phenylchromium tricarbonyl)benzyl alcohol. This alcohol was prepared from the ester as described previously for the *para* isomer, vide supra. Upon recrystallization of the crude product from an ether/pentane mixture, yellow crystals, m.p. 79—81°C were obtained in 80% yield. Infrared analysis [34], (ν, cm^{-1}) revealed ($CHCl_3$): 3580, 3350, 1175 ($-OH$); 1980, 1905 (C≡O); 1600 (phenyl nucleus); 1460 ($>CH_2$?); 900 (isolated hydrogen of *m*-phenylene ?); 785, 740, ~708 (phenyl ?); NMR [35] (CD_3COCD_3): δ(ppm) 7.35—7.0, complex multiplet ($-C_6\underline{H}^A\underline{H}^B\underline{H}^C\underline{H}^D-$); 6.10—5.23, complex multiplet [$(CO)_3$-$CrC_6\underline{H}_5-$] 4.64, singlet ($-C_6H_4-C\underline{H}_2-O-$); 4.5—4.0, very broad ($-O\underline{H}$?). Anal. Found: C, 59.89; H, 3.85; O, 19.74. $C_{16}H_{12}CrO_4$ calcd.: C, 60.00; H, 3.78; Cr, 16.24; O, 19.98% *.

m-(π-Phenylchromium tricarbonyl)benzyl p-toluenesulfonate (V-OTs).

m-(π-Phenylchromium tricarbonyl)benzyl alcohol (0.200 g, 0.625 mmol) and 0.170 g of *p*-toluenesulfonyl chloride was dissolved in 3 ml diglyme (distilled under nitrogen) containing 0.35 ml of 40% aqueous sodium hydroxide. The solution was stirred at room temperature under nitrogen for 16 h. Addition of ice/water to the reaction mixture gave a thick yellow oil. The supernatant solution was decanted and the crude product washed with cold water and dried under vacuum. A crystalline material (0.211 g, 71%) was obtained after stirring the gummy material with ~5 ml of ice-cold ether. The solid was recrystallized from ether/pentane, m.p. 100—102°C. Infrared analysis [34] (ν, cm^{-1}) revealed ($CHCl_3$): 3350 (OH, unreacted s.m. ?); 3090, 3065, 3040 (C—H aromatic); 2965, 2870, 1460, 1380 ($-CH_3$); 2930, ~2850, 1470 ($>CH_2$); 1995, ~1915 (C≡O);

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* We thank Dr. T.L. Maier for help with the preparation of this analytical sample.

1610, 1500 (phenyl nucleus); 1390, 1288, 1273 ($ArSO_2OR'$); 840 (isolated H in *m*-phenylene ?); 815 (three adjacent H's in *m*-phenylene ?); 702 (phenyl ?) NMR [35] (CD_3COCD_3): δ(ppm) 7.85—7.1, complex multiplet (the superposed resonances of the *m*- and the *p*-phenylenes, e.g. $—C_6\underline{H}_4—CH_2—$ and $—C_6\underline{H}_4CH_3$); 6.05—5.4, complex multiplet [$(CO)_3CrC_6\underline{H}_5—$]; 5.11, singlet ($—C_6H_4—C\underline{H}_2—O—$); 2.41, singlet ($—C_6H_4C\underline{H}_3$). Anal. Found: C, 58.10; H, 3.88; O, 20.01; S, 6.76%. $C_{23}H_{18}CrO_6S$ calcd.: C, 58.23; H, 3.82; Cr, 10.96; O, 20.23; S, 6.76.

4'-Nitro-3-biphenylcarbinol. 4'-Nitro-3-biphenylcarboxylic acid, m.p. 233—235°C, was prepared according to the procedure of Dannley and Sternfeld (m.p. 232—233°C) [40] and converted to the corresponding carbinol by an adaptation of a procedure by Brown and Rao [41].

A solution of 0.219 g (1.57 mmol) of anhydrous aluminum chloride in 3 ml of diglyme (distilled from lithium aluminum hydride) was added dropwise to a stirred mixture of 1.34 g (5.49 mmol) of the carboxylic acid and 0.190 g, (5.43 mmol) of sodium borohydride in 6 ml of anhydrous diglyme. After the addition was complete the reaction was allowed to proceed at room temperature for one hour and at 70—75°C for an additional hour. The mixture was poured into a solution of 2 ml of concentrated hydrochloric acid in 20 ml of ice/water. The gummy precipitate which resulted was dissolved in ether and the ether was extracted with 15% sodium hydroxide to remove any unreacted starting material. The ethereal solution was dried (Na_2SO_4) and the solvent evaporated under aspirator vacuum. The residue was recrystallized from ethanol/water to give 0.842 g (66%) of pale yellow product, m.p. 69—71°C. Infrared analysis [34] (KBr) revealed: 3500, 3250 (broad, O—H); 3050 (C—H, aromatic); 2910, 2860 ($—CH_2—$); 1600, 1445 (aromatic nucleus); 1520, 1350 ($—NO_2$), 1030 (—C—OH); 850, 785, 750 (substituted phenyl); NMR [35] (CCl_4) δ(ppm) 8.4—7.8 AB-type quartet, $J_{AB} = J_{A'B'} = 8$ Hz ($—C_6\underline{H}^A\underline{H}^{A'}\underline{H}^B\underline{H}^{B'}—$); 7.7—7.3, complex multiplet (4 H, *meta*-disubstituted phenyl); 4.74, singlet ($—C\underline{H}_2—O$); ~2.8 broad singlet ($O\underline{H}$). Anal. Found: C, 68.27; H, 4.99; N, 6.25%. $C_{13}H_{11}O_3N$ calcd.: C, 68.11; H, 4.84; N, 6.11.

4'-Nitro-3-biphenylcarbinyl p-toluenesulfonate (VI-OTs). A sample of 0.84 g of 4'-nitro-3-biphenylcarbinol was converted to the tosylate in the manner described for II-OTs. Two recrystallizations of the crude product from carbon tetrachloride gave 0.91 g (64%) of pale yellow crystals, m.p. 95—97°C. Infrared analysis (ν, cm^{-1}) showed [34] (KBr): 3050 (C—H, aromatic); 2930(sh), 2900, 2820 (C—H, aliphatic); 1600, 1445 (phenyl nucleus); 1510 (NO_2); 1360 ($RSO_2OR' + NO_2$) 1170 (RSO_2OR'); 1090 (O—R'); 852, 835, 815, 793, 750 (CH, aromatic, out-of-plane bending); NMR [35] ($CDCl_3$): δ(ppm) 8.4—7.2, complex multiplet (12=C—H, aromatic); 5.18 ($—C\underline{H}_2—O—$); 2.43 ($=C—C\underline{H}_3$). Anal. Found: C, 62.63; H, 4.34; N, 3.73; S, 8.43%. $C_{20}H_{17}NO_5S$ calcd.: C, 62.65; H, 4.47; N, 3.65; S, 8.36.

Acetolysis rates were measured titrimetrically using the ampule technique described previously [13]. Deoxygenated solvent [13a] was employed for the complexes. In most cases individual runs were followed through 60—70% reaction and gave first order plots which were linear through at least 50% reaction. Observed rate constants and activation parameters, calculated in the unusual manner are recorded in Table 1. Salt effect "*b*" values computed from runs containing added sodium acetate are recorded in Table 2.

Products from the acetolysis of *p*-(π-phenylchromium tricarbonyl)benzyl *p*-toluenesulfonate (II-OTs) were determined as follows. A solution of 50 mg of II-OTs in 10 ml of deoxygenated, anhydrous acetic acid buffered with 0.05 *M* sodium acetate was heated at 68.5°C for 55 min (~10 half-lives) in a sealed tube under nitrogen. After having been cooled to room temperature the solution was poured into ~70 ml of an ice/water mixture and extracted with three 25-ml portions of ether/pentane (2 : 1). The combined extract was washed twice with excess cold 10% aqueous sodium bicarbonate and with water. After having been dried over anhydrous magnesium sulfate the solution was filtered and concentrated to ~8 ml in a rotary evaporator. A TLC analysis indicated the presence of only one product, R_f 0.36, identical with that of authentic *p*-(π-phenyl chromium tricarbonyl)benzyl acetate but distinctly different from that of *p*-phenylbenzyl acetate, R_f 0.76. The addition of pentane to the cooled solution caused the precipitation of 30 mg (79%) of yellow crystals, m.p. 89—91°C whose infrared spectrum is identical to that of authentic *p*-(π-phenylchromium tricarbonyl)benzyl acetate, m.p. 90—92°C, vide supra.

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