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SIDE-CHAIN REACTIONS IN π-CHROMIUM TRICARBONYL COMPLEXED ARENES

II*. ELIMINATION FROM (2-PHENYLETHYL TOSYLATE)- AND (2-PHENYLETHYL BROMIDE)–CHROMIUM TRICARBONYL IN THE REACTION WITH ETHANOLIC SODIUM ETHOXIDE

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SUMMARY

The rates of elimination with sodium ethoxide in ethanol of the (2-phenylethyl bromide)chromium tricarbonyl and of the (2-phenylethyl *p*-toluenesulphonate)-chromium tricarbonyl were determined over a range of temperatures. The substrates gave the complexed styrene in 100% (Br) and 97% (OTs) yield. For comparison the rate of elimination of the uncomplexed 2-phenylethyl and 2-(*p*-nitrophenyl)ethyl bromides and tosylates were measured. Complexation strongly increases the rate of elimination, although the effect is much less marked than that of a *p*-nitro group. The reasons for the kinetic non-equivalence between $Cr(CO)_3$ and *p*-NO_2 groups are discussed.

INTRODUCTION

There is strong evidence, both thermodynamic[2] and kinetic[1,3], for the remarkable capacity of chromium tricarbonyl complexed with an arene to stabilize a positively-charged α-carbon atom. On the other hand, the π-chromium tricarbonyl group has been quantitatively compared to a *p*-nitro group in its electron-withdrawing power[4]***. Interpretation of these effects is still a matter of discussion. By analogy with

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[*] For Part I see ref. 1.

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[***] The comparison between the electron-attracting power of $Cr(CO)_3$ and *p*-nitro groups is based mainly upon the similar pK_a values found for *p*-nitro and π-chromiumtricarbonyl substituted phenylacetic acids[4a] and on the similar rate constants of hydrolysis for the substituted benzoic esters[4b]. The validity of both these comparisons is open to discussion: In a recent paper[5] a referee has suggested that the acidity of the complexed phenylacetic acid may be lowered by intramolecular hydrogen bonding to either the chromium or one of the carbonyls. As far as the hydrolysis is concerned, a steric effect of the bulky π-bound chromium tricarbonyl, even if not dominant, could alter the value of the rate of saponification of methyl benzoate. A discussion of steric effects is practically precluded by lack of kinetic data on different types of reactions. Studies are in progress in our laboratory to provide evidence for or against such an effect.

the α-ferrocenyl compounds, the increased reactivity (10^4–10^5) in solvolysis of benzyl derivatives has been interpreted as a direct interaction of a filled *d*-orbital of the metal with the empty *p*-orbital of the carbon in the transition state, or as a metal–carbon hyperconjugation (σ–π delocalization)[3,5]. The strong electron-withdrawal effect, on the other hand, is interpreted as occurring mainly through the π-orbitals of the benzene ring[4b,6,7], or alternatively, is attributed to an inductive effect involving the σ-skeleton of arene[8]. In few other systems have so many quantitative studies been carried out as in the styrene-forming elimination from 2-phenylethyl systems,

Within the concept of a continuous spectrum of transition state structures of base-induced E_2 reactions, 2-phenylethyl systems involve development of strong carbanion character at the α-carbon (E_{1cB}-like transition state)[9]. Particularly efficient in accelerating the reaction rate are electron-withdrawing groups which stabilize, by inductive and/or resonance effects, the increased negative charge on the α-carbon. In view of the peculiar properties of $Cr(CO)_3$ group we chose to study the rates of elimination from π-chromium tricarbonyl 2-phenylethyl bromides and tosylates with the objective of elucidating the effect of the group on the charge distribution at the transition state.

RESULTS AND DISCUSSION

(2-Phenylethyl tosylate)- and (2-phenylethyl bromide)–chromium tricarbonyl were prepared by conventional procedures (see Experimental). Styrenechromium tricarbonyl was made as described by Rausch *et al.*[10].

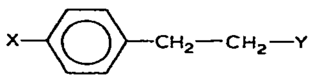
The reaction was carried out in absolute ethanol containing sodium ethoxide, and followed acidimetrically. Olefin yields were calculated from the absorption, after more than 10 half-lives, of the reaction mixtures at 450 nm, at which the reagents do not absorb appreciably. The molar extinction coefficient of the complexed styrene at this wavelength is 417. Styrene does not decompose under the conditions used.

To provide accurate comparisons, rates for the unsubstituted and the *p*-nitro bromides and tosylates have also been measured. The eliminations from the unsubstituted compounds were followed acidimetrically, while those for the *p*-nitro bromide and tosylate were, because of the high speed of the reaction, followed by spectrophotometric determination of the *p*-nitro styrene produced (λ_{max} 302 nm, $\varepsilon = 1.3 \times 10^4$). A large excess of the base over the substrate was used in these runs and pseudo-first-order rate constants were calculated from the slope of a plot of log (D_∞–D_t) against time. The reactions were all cleanly second order.

The rate constants for elimination from 2-phenylethyl bromide and tosylate are in good agreement with those previously reported by other authors[11,12]. Less satisfactory agreement was found in the case of the rates and activation parameters for the *p*-nitro bromide, the earlier data for which, as the authors themselves wrote[11], suffered from large uncertainty due to the high speed of reaction, which was followed acidimetrically at only two temperatures. No data were available for the elimination of the *p*-nitro tosylate in this particular solvent–base system. Rate constants, olefin

TABLE 1

OLEFIN YIELDS, RATE CONSTANTS (k_{el}) AND ACTIVATION PARAMETERS FOR ELIMINATIONS FROM 2-PHENYLETHYL BROMIDES AND TOSYLATES,



$X-C_6H_4-CH_2-CH_2-Y$

IN THE REACTION WITH SODIUM ETHOXIDE IN ABSOLUTE ETHANOL[a]

No.	Substrate[a] X	Y	Temp. (±0.1°C)	Styrene yield (%)	$k_{obs}\times 10^{3b}$ ($l\cdot m^{-1}\cdot sec^{-1}$)	$k_{el}\times 10^{3c}$ ($l\cdot m^{-1}\cdot sec^{-1}$)	$\Delta H^{\neq d}$ (kcal/mole)	$\Delta S^{\neq d}$ (e.u.)
(I)	H	Br	60.0			8.90		
			50.2	100±0.3		3.31	19.4	−10.1
			40.0			1.20		
(II)	NO_2	Br	39.9			2370		
			30.0	100±0.5		1090	14.2	−11.4
			24.1			680		
(III)	π-$Cr(CO)_3$	Br	36.0			29.8		
			30.1	100±0.3		16.6	18.9	−4.3
			22.5			7.1		
(IV)	H	OTs	50.0		0.99	0.38		
			40.5	38±0.5	0.43	0.16	20.2	−12.0
			30.0		0.12	0.04		
(V)	NO_2	OTs	39.9			643		
			29.8	100±0.3		301	15.0	−11.4
			23.0			155		
(VI)	π-$Cr(CO)_3$	OTs	41.8		30.0	29.1		
			32.8	97.0±0.4	11.0	10.7	19.7	−3.2
			26.0		5.10	4.95		

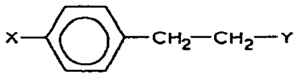
[a] Substrate: 0.02–0.05 *M*; base: 0.02–0.1 *M*. The ionic strength was kept constant by adjusting to 0.1 *M* with $NaClO_4$. For II and V the substrate concentration was $1–1.3\times 10^{-4}$ *M* and the base $2–3\times 10^{-3}$ *M*. [b] Mean values of two or three different runs. Deviations were within the limits of experimental error. [c] $k_{el}=k_{obs}\times$ % olefin. [d] At 30°.

yields, and activation parameters are listed in Table 1.

The conversion to olefin is quantitative for the elimination from all bromides, whereas it varies from 38 to 100% with the tosylates. The increase in olefin percentage is commonly observed when electron-withdrawing substitutents are present in the ring: *e.g.* in the tosylates it varies from 20 to 67% on passing from *p*-methoxy to *m*-bromo under the same conditions[12]. The $Cr(CO)_3$ group thus must be regarded as a strong electron-withdrawing group, although the occurrence of a small (3%) but definite amount of substitution, absent in the case of the *p*-nitro tosylate, indicates that the $Cr(CO)_3$ and *p*-NO_2 groups do not have identical effects. The marked quantitative difference between the capacities of the $Cr(CO)_3$ and *p*-nitro groups to promote the elimination is made clear in Table 2.

For the tosylates and the bromides the complexing strongly increases the rate of elimination, although the extent of the acceleration is not the same in both cases: $[k_{Cr(CO)_3}/k_H]=142$ (Y=OTs), $[k_{Cr(CO)_3}/k_H]=37$ (Y=Br). This difference in the rate enhancement probably originates in the different amount of negative charge present in the transition state in the two series; *e.g.* the value of the Hammett reaction constant, ρ, is +2.14 for bromides[11] and +2.50 for tosylates[12] under identical conditions.

TABLE 2

RELATIVE RATES OF ELIMINATION FROM  IN ABSOLUTE ETHANOL CONTAINING SODIUM ETHOXIDE AT 40°

X	*Y*	$k_{el} \times 10^3$ $(l \cdot m^{-1} \cdot sec^{-1})$	*Rel. rates*
H	OTs	0.16	1
$Cr(CO)_3$	OTs	22.6	142
NO_2	OTs	643	4020
H	Br	1.20	7.5
$Cr(CO)_3$	Br	44.6	270
NO_2	Br	2370	14800

The results of Table 2 provide unequivocal evidence of a substantial difference between the kinetic effects of a $Cr(CO)_3$ group and a p-NO_2 group; the rate ratio $k_{p\text{-}NO_2}/k_H$ is 4020 for the tosylates and 1970 for the bromides.

A priori at least two factors can be responsible for the decrease in the activating effect on going from p-NO_2 to $Cr(CO)_3$: (*a*) steric hindrance to the approaching base because of the bulkness of the $Cr(CO)_3$ group; and (*b*) lower capacity of the chromium tricarbonyl to stabilize the developing negative charge at the α-carbon. Some of our recent results[13] suggest that steric effects, which are of little importance in uncomplexed series, can become significant for S_N2 reactions at the benzylic carbon in complexed arenes. Complexation, in fact, decreases to a small extent (2–3 times) the rate of substitution. In elimination a rather large (6–8 e.u.) increase in the entropy term is observed on complexing, showing that the attack at the benzylic hydrogen by base cannot be governed by steric factors. Since electronic rather than steric factors are thus involved, one can compare the electron attracting capacities of a $Cr(CO)_3$ group and a p-NO_2 group by calculating the σ values by use of the reaction constants ρ. The values are:

$$\sigma(Cr(CO)_3) = +0.85\ (OTs),\ +0.74\ (Br);\ \sigma(p\text{-}NO_2) = +1.45\ (OTs),\ +1.53\ (Br)^{\star}$$

The mean value of $\sigma(Cr(CO)_3) = +0.79$ is quite close to the ordinary Hammett σ-constant for the p-NO_2, +0.778, which is known not to fit the Hammett correlations in those reactions in which an unshared electron pair on an atom next to benzene ring is involved. The much enhanced effect of the p-NO_2 group, which is reflected in the elevated σ-value (mean value +1.49)[**], arises from direct resonance interaction between the negative charge on the α-carbon and the substituent in the transition state. Such extra stabilization by resonance is absent when $Cr(CO)_3$ is involved,

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[*] The same value is obtained by using the data from ref. 11.

[**] This value is higher than $\sigma^-(p\text{-}NO_2) = 1.27$[14]. It should be noted, however, that σ^- values are derived from the reactions of ionization of phenols and anilines, where the reaction center is a heteroatom. The difference reflects a greater ability of the group to delocalize a negative charge present on carbon.

showing that the transmission of the electronic effect through the ring involves mainly the σ-framework rather than the π-electron cloud. The activation parameters support this interpretation. Thus, while for the *p*-nitro derivatives the increase in rate is due almost entirely to a lower enthalpy of activation (5.2 kcal in both series), in the $Cr(CO)_3$ substrates the increased reactivity depends mainly on a less negative entropy of activation (6–8 e.u.), $\Delta H^{\neq}$ being not very different from that for the unsubstituted compounds. It, thus, appears that when direct resonance interaction is the major factor the effect is enthalpic while an inductive effect is represented by a change of entropy. Such an observation is not new since it is known that Hammett σ's reflect entropy rather than enthalpy changes[15], whereas substituents capable of strong resonance interaction show a pattern in the $\Delta H^{\neq}$–$\Delta S^{\neq}$ diagram in which rather small changes in entropy correspond with large changes in energy of activation, indicating that σ-constants mainly reflect enthalpy effects[16].

Our results are not in conflict with the previous reports of the equivalence between $Cr(CO)_3$ and p-NO_2[4], since the reactions studied previously did not involve direct resonance interaction between the reaction center and the substituent. Our results do however, conflict with the current view that the π-complexed chromium tricarbonyl group is capable of strong electron withdrawal by resonance*[6,7]. On the basis of different reasoning, Gubin *et al.*[8] have recently suggested that "... with regard to the π-electron density in the ligand there should be no significant change in its reactivity upon its coordination with the metal. Substantial changes in the ligand reactivities are governed by a varying ring σ-framework effective charge upon coordination". Our results seem to be in line with this view.

As far as the transition state structure of complexed 2-phenylethyl derivatives is concerned, the rate ratio k_{OTs}/k_{Br} can be used to give a measure of the extent of C_β–Y bond breaking in substitutions and eliminations, since k_{OTs}/k_{Br} is thought to increase with increasing C–Y bond breaking[18]. In 2-phenylethyl systems the progressive rise of k_{OTs}/k_{Br} with increasing electron-withdrawing power of the aromatic substituent has been interpreted[19] as representing an increase in the degree of C–Y bond breaking induced by an increase in C_α–H bond breaking, which would represent a paradox for an E_{1cB} mechanism. As an alternative, Cockerill[20] interpreted an increase in the ratio, for example from 0.15 for *p*-methoxy to 1.57 for *p*-nitro in tert-butyl alcohol with tert-butoxide, as an increase in C–H breaking arising from a decrease in C–Y bond breaking. The rate ratios calculated from our results and from literature data for the reaction in ethanol with sodium ethoxide are as follows: p-OCH_3, 0.065[19]; H, 0.13; p-NO_2 = 0.27; $Cr(CO)_3$ = 0.52. On the basis of Cockerill's suggestion, complexing must shift the transition state structure towards a well-advanced carbanion character [E_{1cB}-like] by diminishing the extent of C–Y bond breaking. However the fact that k_{OTs}/k_{Br} is larger for the $Cr(CO)_3$ than for p-NO_2 group, despite a smaller electron-attracting power, makes this interpretation rather ambiguous and it can hardly be used as a mechanistic criterion in this case. In complexed substrates

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* A crucial point is the difference between $\sigma(Cr(CO)_3) = +0.79$ found in our reaction and that calculated from pK_a of π-(phenol) chromium tricarbonyl in water, *viz.*[5] $\sigma = +1.6$. Steric inhibition to solvation is one of the reasons invoked for the increased acidity of 2,6 substituted phenols, and a value of $\sigma(p\text{-}NO_2)$ as high as +1.44 was calculated for 2,6 di-tert-butyl-*p*-nitrophenol[17]. However, such hindrance, even if present, seems hardly likely to be responsible for the difference observed.

some other factors are probably responsible for the greater increase of the reactivity for the tosylate compared with that for the bromide.

EXPERIMENTAL

Melting points are uncorrected. Microanalyses are by Dr. E. Celon, Istituto di Chimica Organica, Padova (Italy).

Preparation of the 2-phenylethyl bromide and p-toluenesulphonate

2-Phenylethyl alcohol and bromide were redistilled commercial materials. The tosylate was prepared from the corresponding alcohol by Tipson's method[21]. M.p. 38–39° (lit.[12] 38.5–39°).

2-(p-Nitrophenyl)ethyl bromide

2-(*p*-Nitrophenyl)ethyl bromide was obtained by nitration of 2-phenylethyl bromide with nitric acid in acetic anhydride. M.p. 69°C (lit.[22] 69–70°).

2-(p-Nitrophenyl)ethyl tosylate

2-(*p*-Nitrophenyl)ethyl tosylate was prepared by the method described by Hoffmann[23] from 2-(*p*-nitrophenyl)ethyl bromide and freshly-prepared silver toluene *p*-sulphonate in acetonitrile. Recrystallization from chloroform gave crystals, m.p. 125–126° (lit.[23] 126–127°). A second recrystallization from acetone/light petroleum gave crystals, m.p. 132.5–133.5°.

(2-Phenylethanol)chromium tricarbonyl

The complex was made by heating hexacarbonylchromium with 2-phenylethanol under reflux in the apparatus described by Strohmeier[23] until no more hexacarbonyl sublimed out (4–5 h). A nitrogen atmosphere was maintained during the reaction and in all subsequent operations. After cooling, the residual alcohol was distilled out under reduced pressure (0.05 mm) and the residue diluted with ether and filtered through deactivated alumina. Crystallization from ether/light petroleum gave a yellow product in 60% yield. M.p. 55–56° (Found: C, 50.86; H, 3.80. $C_{11}H_{10}CrO_4$ calcd.: C, 51.16; H, 3.90%.) IR analysis showed ($CHCl_3$) 3580 and 3450 (OH); 3010 (CH phenyl); 2860 (CH aliphatic); 1960, 1840 cm^{-1} (C≡O).

(2-Phenylethyl p-toluenesulphonate)chromium tricarbonyl

Method a. The complexed alcohol was treated with *p*-toluenesulphonyl chloride in pyridine at −10° [21]. The crude product was dissolved in benzene, filtered through deactivated alumina, and recrystallized twice from ether/light petroleum. Yield 40%. M.p. 122–123°. (Found: C, 52.50; H, 3.86; S, 7.70. $C_{18}H_{16}CrO_6S$ calcd.: C, 52.42; H, 3.94; S, 7.77%.) IR analysis showed ($CHCl_3$) 3005 (CH phenyl); 2940 (CH aliphatic); 1960, 1840 (C≡O): 1360, 1185, 1175 cm^{-1} ($-OSO_2-$). UV (C_2H_5OH): 235 nm (ε=6500), 255 nm (5900), 315 nm (6800).

Method b. A higher yield (ca. 70%) was obtained by direct treatment of 2-phenylethyl-OTs with $Cr(CO)_6$ in n-butyl ether. 2-Phenylethyl-OTs (0.029 moles) and 0.03 moles of $Cr(CO)_6$ in 100 ml of n-butyl ether were heated under nitrogen at 150° (30 h). After cooling the solution was filtered, the solvent was removed at reduced pressure, and the solid residue was recrystallized from n-heptane. The product had the same physical characteristics as that prepared by method *a*.

(2-Phenylethyl bromide)chromium tricarbonyl

(2-Phenylethyl-OTs)chromium tricarbonyl (9.8×10^{-3} moles) and 4×10^{-2} moles of LiBr were dissolved in 40 ml of anhydrous acetone previously deaerated with N_2. The solution was kept in the dark for three days. The acetone was evaporated and the residue dissolved in ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated, and the residue crystallised from ether/light petroleum. Yield 80%, m.p. 68°. (Found: C, 41.22; H, 2.90; Br, 24.80. $C_{11}H_9$-$BrCrO_3$ calcd.: C, 41.15; H, 2.80; Br, 24.90%.) IR analysis showed ($CHCl_3$) 3000 (CH phenyl); 2980 (CH aliphatic); 1960, 1840 cm^{-1} (C≡O).

Styrenetricarbonylchromium

The method used was that suggested by Rausch *et al.*[10]. Orange crystals were obtained after sublimation m.p. 78–79° (lit.[10] 78–79°). Elemental analysis and spectral characteristics were corrected.

Kinetic measurements

The reactions were carried out in a 100 ml flask from which aliquots could be withdrawn under nitrogen. The solution of the substrate was allowed to equilibrate thermally, while a current of pre-saturated nitrogen was bubbled through, and then a small volume of concentrated base was added. 5 ml aliquots were poured into an excess of HCl and the solution was then titrated against NaOH. For substrates (II) and (V), the base was introduced from a microsyringe into a 10 mm silica cell of a Unicam SP 800 Spectrophotometer filled with the substrate solution. The formation of 4-nitrostyrene was followed at 302 nm. Extinction coefficients were measured with a Cary 14 model spectrophotometer.

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