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SIDE-CHAIN REACTIONS IN π-CHROMIUM TRICARBONYL-COMPLEXED ARENES

IV*. SOLVENT AND DEUTERIUM ISOTOPE EFFECTS IN *E*2 REACTIONS OF SOME 2-PHENYLETHYL AND 1-PHENYL-2-PROPYL DERIVATIVES

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Summary

The rates and products of elimination with sodium ethoxide in ethanol, and potassium t-butoxide in t-butanol, of chromium tricarbonyl-complexed (2-phenylethyl bromides), (2-phenylethyl tosylates), (1-phenyl-2-propyl bromides), and (1-phenyl-2-propyl tosylates) were determined. Complexation increases the rate of elimination, the size of the effect depending on leaving group, solvent/base system and, to a minor extent, structure. The $Cr(CO)_3$ group increases the olefin percentage when substitution competes with elimination, whereas the relative proportions of the olefin isomers obtained from secondary substrates are practically unchanged whether the ring is complexed or not. Deuterium isotope effects have been measured for the elimination from uncomplexed, complexed and 2-(*p*-nitrophenyl)ethyl compounds. The magnitude of the isotope effect does not vary appreciably with substituents.

Introduction

Kinetic data are now available for a number of side-chain reactions of an arene ligand, Ar—R, complexed with $Cr(CO)_3$, showing that the effect of complexation on reactivity differs and sometimes acts in opposite directions. This versatile behaviour is made clear if one considers different reactions, as follows:

(a). S_N1 reactions. Reactions in which the α-carbon has a carbonium ion-like structure in the transition state are strongly accelerated by the presence of the metal carbonyl group. Ionization reactions of benzyl derivatives, i.e.

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* For part III see ref. 1.

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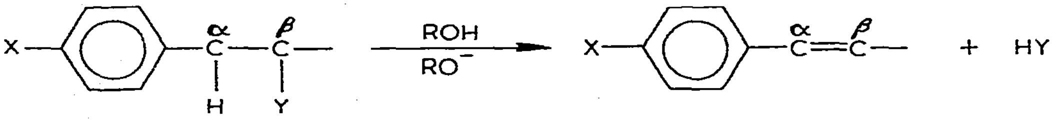
solvolysis of chlorides [2] or isomerization of thiocyanates to isothiocyanates [3], are accelerated by a factor of 10^4—10^5. This extraordinary electron-donating effect of the $Cr(CO)_3$ group has been interpreted as a direct interaction of a filled *d*-orbital of the metal with the empty *p*-orbital of the carbon (back-bonding), or as a metal—carbon hyperconjugation (σ—π delocalization) [2, 4, 5].

(b). S_N2 reactions. In S_N2 displacement reactions at saturated carbon in aprotic solvents the overall influence of the $Cr(CO)_3$ group varies as one changes the site of nucleophilic attack, i.e. from the α to β carbon atom. In the substitution of chloride by thiocyanate in 2-phenylethyl chlorides in acetone (β attack), the rate increases on complexation by a factor very close to that of a *p*-nitro group, ($k_{Cr(CO)_3}/k_H = 2.3$; $k_{p\text{-}NO_2}/k_H = 2.7$) [1]. This agrees well with the observation of identical pK_a values for complexed phenylacetic acid and *p*-nitrophenylacetic acid [6], showing that the π-chromium tricarbonyl group withdraws electrons as strongly as a *p*-nitro group. However, when the same reaction is carried out at the α-carbon on benzyl chlorides under identical conditions, the rate decreases ($k_{Cr(CO)_3}/k_H = 0.30$) [1]. Analogously, chromium tricarbonyl—benzoic acid is appreciably weaker than the *p*-nitro acid [6]. In both cases decreased reactivity has been interpreted as being due to steric effects of the bulky $Cr(CO)_3$ which may hinder the solvation of the products or the approach of the attacking nucleophile.

(c). E2 reactions. Base catalyzed 1,2 eliminations from 2-phenylethyl compounds to give styrene in alcohols are useful for the examination of the mechanism through which the electron-withdrawing power of the metal carbonyl group takes place. In the transition state of these reactions the α-carbon has a carbanion-like character [7] and the excess negative charge can be delocalized by inductive and/or by resonance effects in the ring system. The results of elimination from 2-phenylethyl bromides and tosylates in ethanol with sodium ethoxide [8] provided evidence of a substantial difference between the kinetic effects of a $Cr(CO)_3$ and a *p*-nitro group when, as in this case, direct resonance between the reaction centre and the substituent is feasible. The data suggest that the nature of the electron-withdrawing effect is almost inductive and the capacity of the $Cr(CO)_3$ to delocalize a negative charge by resonance very slight. This contrasts with the generally accepted idea that the metal group withdraws electron density by resonance and that its power is even greater than that of a *p*-nitro group [5, 9]. As a consequence, there should be very little change in the π-electron character in the arene upon complexation and changes in the ligand reactivities should be goverend by a varying σ-framework charge [10].



To elucidate these controversial aspects we extended our studies on elimination reactions. In this paper we report rates, base-solvent, kinetic isotope and structural effects for some 2-phenylethyl- and 1-phenyl-2-propyl-tosylates and -bromides.

Results and discussion

(2-Phenylethyl *p*-toluenesulphonate)chromium tricarbonyl can be obtained either by direct reaction of the ester with chromium hexacarbonyl in n-butyl ether or by previous complexation of the 2-phenylethyl alcohol and subsequent reaction of the complexed alcohol with *p*-toluenesulphonyl chloride in pyridine. The first method gave higher yields [8]. We have prepared uncomplexed primary tosylates, both deuterated and undeuterated, by usual procedures. The complexation was then accomplished with $Cr(CO)_6$. 2-Phenylethyl bromides have been obtained from the tosylates by direct displacement with lithium bromide in acetone.

When the same procedure was applied to secondary 1-phenyl-2-propyl tosylate, the crude product of direct complexation was a mixture of complexed olefins with only small amounts of complexed tosylate. By chromatography on a silica gel column a yellow product was obtained, which IR, NMR and GLC analysis showed to be a mixture of 3-(phenylchromium tricarbonyl)-1-propene and *cis*- and *trans*-1-(phenylchromium tricarbonyl)-1-propene. The relative proportions estimated by GLC were: 3-phenyl-1-propene 18%, *trans*-1-phenyl-1-propene 76%, *cis*-1-phenyl-1-propene 6%. Nearly identical percentages (19, 71, 10) have been obtained when the uncomplexed tosylate was reacted under the same conditions and for the same reaction time in the absence of $Cr(CO)_6$. Thus the complexed olefins might be formed by previous elimination of uncomplexed tosylate and subsequent reaction of $Cr(CO)_6$ with the olefins or by previous complexation of the tosylate which subsequently eliminates to give the complexed olefins. In any case the method of direct complexation of secondary 1-phenyl-2-propyl tosylate in n-butyl ether cannot be utilized to give the complexed tosylate which was prepared from the complexed secondary alcohol with *p*-toluenesulphonyl chloride.

In Tables 1 and 2 the rates and olefin yields of elimination of 2-phenylethyl tosylates and bromides and their deuterated analogs are reported for both ethoxide/ethanol and t-butoxide/t-butyl alcohol solution. Table 3 reports the rates and the relative proportions of the three isomeric olefins formed from 1-phenyl-2-propyl tosylate and bromide in the same solvent/base systems.

Effect of complexation

(a). On rates. The effect of complexing the phenyl ring with $Cr(CO)_3$ on the rate of elimination, as measured by $k_{Cr(CO)_3}/k_H$, is reported in Table 4 together with the ratios $k_{p\text{-}NO_2}/k_H$.

It is clear that complexed tosylates and bromides, both primary and secondary, eliminate with higher rate constants (11—495 fold) than the uncomplexed analogs in all solvent/base systems. The size of the effect depends greatly on leaving group, solvent, and to a minor extent on structure.

The strong electron-withdrawing effect of the $Cr(CO)_3$ is responsible for the increase of rate by stabilizing the partial negative charge at the transition state. It is striking that tosylates are more sensitive than bromides to the presence of the complexing group. As tosylates utilize transition state structures with more carbanion-like character than bromides [7], the greater the amount of negative charge at the α-carbon the greater will be the effect of complexation.

TABLE 1

OLEFIN YIELDS AND RATE CONSTANTS (k_{el}) FOR ELIMINATIONS FROM 2-ARYL BROMIDES AND TOSYLATES. $XC_6H_4CZ_2CH_2Y$, IN THE REACTION WITH SODIUM ETHOXIDE IN ABSOLUTE ETHANOL AT 39.9°.

Substrate [a]			Styrene [b] yield (%)	$k_{el} \times 10^4$ [c] ($l \cdot m^{-1} \cdot s^{-1}$)	Isotope effect k_H/k_D
X	Z	Y			
H	H	Br	100	12.9	6.79 ± 0.19 [d]
H	D	Br	100		
π-$Cr(CO)_3$	H	Br	100	641	7.70 ± 0.31
π-$Cr(CO)_3$	D	Br	100	83	
NO_2	H	Br	100	28200	7.92 ± 0.16
NO_2	D	Br	100	3560	
H	H	OTs	38	1.5	5.40 ± 0.52 [d]
H	D	OTs	9.7		
π-$Cr(CO)_3$	H	OTs	97	297	5.50 ± 0.13
π-$Cr(CO)_3$	D	OTs	75	54	
NO_2	H	OTs	100	7100	5.90 ± 0.14
NO_2	D	OTs	100	1204	

[a] Base: 0.04—0.1 *M*; for the *p*-nitro compounds: 0.002—0.003 *M*. [b] Each figure is the average of two different determinations. Deviations were within the experimental error (2%). [c] Mean values of two or three different runs. Deviations were within the experimental error (3%). Some k_{el} values of the undeuterated compounds are slightly different from those previously reported [8]. This might be due to the different technique used for evaluating the concentration and/or to the different operator. [d] From ref. 25. The value of k_{el} for the undeuterated compound has been checked to be the same of that reported in ref. 25.

However, from Table 4 it appears that the effectiveness of the electron-attracting power of $Cr(CO)_3$ is much lower than that of the *p*-nitro group, which is at least one order of magnitude more effective in both solvents for both leaving groups. The equivalence between the two groups has been shown in reactions where there is no direct resonance between the reaction centre and the substituent by both kinetic [1] and thermodynamic data [6]. The non-kinetic equivalence which occurs in *E*2 reactions of 2-phenylethyl derivatives, where direct resonance takes place, is interpreted by us as a consequence of the

TABLE 2

OLEFIN YIELDS AND RATE CONSTANTS (k_{el}) FOR ELIMINATIONS FROM 2-ARYLETHYL BROMIDES AND TOSYLATES. $XC_6H_4CZ_2CH_2Y$, IN THE REACTION WITH POTASSIUM tert-BUTOXIDE IN tert-BUTANOL

Substrate [a]			Styrene [b] yield (%)	$k_{el} \times 10^4$ [c] ($l \cdot m^{-1} \cdot s^{-1}$)	Isotope effect k_H/k_D
X	Z	Y			
H	H	Br	100	219	7.42 ± 0.25
H	D	Br	100	29.5	
π-$Cr(CO)_3$	H	Br	100	2330	7.44 ± 0.32
π-$Cr(CO)_3$	D	Br	100	314	
NO_2	H	Br	100	98000	8.85 ± 0.40
NO_2	D	Br	100	11070	
H	H	OTs	100	40.1	7.50 ± 0.30
H	D	OTs	86	5.3	
π-$Cr(CO)_3$	H	OTs	100	11100	8.88 ± 0.70
π-$Cr(CO)_3$	D	OTs	100	1250	
NO_2	H	OTs	100	108000	7.77 ± 0.39
NO_2	D	OTs	100	13900	

[a] Base: 0.04—0.1 *M*; for the *p*-nitro compounds: 0.001—0.003 *M*. [b] Each figure is the average of two different determinations. Deviations were within the experimental error (2%). [c] Mean values of two or three different runs. Deviations were within the experimental error (3%).

TABLE 3

OLEFIN YIELDS AND RATE CONSTANTS (k_{el}) FOR ELIMINATIONS FROM 1-ARYL-2-PROPYL BROMIDES AND TOSYLATES, $XC_6H_4CH_2CH(CH_3)Y$, IN THE REACTION WITH SODIUM ETHOXIDE IN ETHANOL AND POTASSIUM tert-BUTOXIDE IN tert-BUTANOL AT 39.9°.

Substrate [a]		Solvent	Olefin [b] yields (%)	$k_{el} \times 10^4$ [c] ($l \cdot m^{-1} \cdot s^{-1}$)	1-Aryl-1-propene		3-Aryl-1-propene
X	Y				*cis*	*trans*	
H	Br	EtOH	100	4.8	2.8	96.5	0.7
π-$Cr(CO)_3$	Br	EtOH	100	221	2.7	95.4	1.9
H	Br	t-BuOH	100	51	1.1	98.7	0.2
π-$Cr(CO)_3$	Br	t-BuOH	100	631	2.7	97.2	0.1
H	OTs	EtOH	90.7	1.4	8.4	79.2	3.1
π-$Cr(CO)_3$	OTs	EtOH	100	67.5	8.2	86.0	5.8
H	OTs	t-BuOH	100	4.4	4.8	93.6	1.6
π-$Cr(CO)_3$	OTs	t-BuOH	100	2170	2.3	97.3	0.4

[a] Base: 0.05—0.06 *M*. [b] Each figure is the average of two different determinations. Deviations were within the experimental error (2%). [c] Mean values of two or three different runs. Deviations were within the experimental error (3%).

slight ability of the $Cr(CO)_3$ group to delocalize the incipient negative charge by resonance whereas *p*-nitro affects the rate by both its inductive and resonance effects*.

Steric instead of electronic factors could be invoked for the lower activating power of chromium tricarbonyl with respect to the *p*-nitro group. The presence of a bulky group such as $Cr(CO)_3$ might decrease the rate by hindering the approach of the nucleophile, especially t-butoxide, or the solvation of the leaving group. Our data do not provide any evidence for the predominance of such an effect. For bromides the decrease of $k_{Cr(CO)_3}/k_H$ by changing from sodium ethoxide to potassium t-butoxide (Table 4) cannot be attributed to incursion of steric factors since an analogous decrease is observed for the $k_{p\text{-}NO_2}/k_H$ ratio for which no steric effect can be invoked. On the other hand, the effect of complexation, $k_{Cr(CO)_3}/k_H$, is greater in t-butanol than in ethanol for tosylates, a trend opposite to that one would expect for the intervention of steric factors.

The change of the ratio $k_{Cr(CO)_3}/k_H$ with solvent can be rationazlied better on the basis of different transition state geometry being used by bromi-

TABLE 4

RELATIVE RATES OF ELIMINATION AT 39.9°

Substrate	Y	Solvent	$k_{Cr(CO)_3}/k_H$	$k_{p\text{-}NO_2}/k_H$
$PhCH_2CH_2Y$	Br	EtOH	50	2180
	Br	t-BuOH	11	450
	OTs	EtOH	198	4700
	OTs	t-BuOH	276	2700
$PhCH_2{-}\overset{\overset{CH_3}{\vert}}{C}HY$	Br	EtOH	44	
	Br	t-BuOH	12	
	OTs	EtOH	49	
	OTs	t-BuOH	495	

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* The equivalence between the inductive electron-attracting capacities of the two groups is more evident if one calculates the values by use of the known [11] reaction constant ρ's. The mean value of σ calculated for $Cr(CO)_3$, $\sigma_{Cr(CO)_3} = +0.80$, is quite close to the ordinary Hammett σ constant for the p-NO_2, +0.778.

des and tosylates and, consequently, to the different sensitivity to substituents of the two substrates on passing from one medium to the other. It is striking in this respect that Hammett ρ's which measure the amount of negative charge at the α-carbon at the transition state have lower values in t-butanol than in ethanol for bromides, while the reverse is true for tosylates [11].

(b). On reaction products. As shown in Table 1, complexed deuterated and undeuterated primary tosylates give higher yields of styrene than the uncomplexed analogue, especially in ethanol. Elimination is clearly favoured with respect to substitution by the presence of the strongly electron-withdrawing $Cr(CO)_3$. However, the occurrence of a definite amount of substitution for complexed compounds (i.e. 25% for deuterated 2-phenylethyl tosylate in ethanol) makes these substrates different from the *p*-nitro substituted ones, for which the yield of styrene is always 100%. Thus, a *p*-nitro group has a higher capacity to promote the elimination than $Cr(CO)_3$.

For secondary derivatives (Table 2), 1-aryl-1-propene and 3-aryl-1-propene are the only products with but one exception (10% of ether is present for R—OTs in ethanol). 1-Aryl-1-propene (*cis* and *trans*) is largely predominant (98—99%) and the relative proportions of the isomers do not change appreciably with leaving group, solvent and, importantly, whether the phenyl ring is complexed or not. If steric factors were important in determining the product distribution [13], the increase in the bulkiness of the base (from ethoxide to t-butoxide), of the β-substituent (from phenyl to phenylchromium tricarbonyl) and finally of the leaving group (from bromide to tosylate) should favour a lesser predominance of Saytzeff orientation. On the contrary, uncomplexed bromide in ethanol and complexed tosylate in t-butanol gave a very similar product distribution. On the evidence at hand, it seems that steric factors do not govern the product distribution at all.

Alternatively, on the assumption that the Hoffmann/Saytzeff ratio is governed by electronic factors, it has been suggested [14] that an increase in the ratio is indicative of an increase in the ratio of C—H to C—X stretching. Our data on the constancy of the olefin proportions indicate that either the C—H/C—X ratio (i.e. the transition state geometry) is not changing on complexation or that possible changes are not being reflected in the value of the Hoffmann/Saytzeff ratio.

(c). Hydrogen—deuterium isotope effect. In the continuous spectrum ranging from carbanion-like (*E1cb*-like) to carbonium-like (*E1*-like) extremes used in bimolecular eliminations [7], 2-phenylethyl compounds utilize transition state structures having some carbanion character (from central to *E1cb*-like). The structure is shifted towards one or other side of the spectrum by changing, (*a*) the leaving group, (*b*) the strength of the base, (*c*) the acidity of the α-hydrogens [15]. According to theoretical arguments based on the three-centre model, the magnitude of the deuterium isotope effect in proton transfer reactions should be a maximum when the structure of the transition state is symmetrical (proton equally transferred between the carbon and the base) whereas lower values should correspond to asymmetrical transition states (carbonium ion-like and carbanion-like structures) [16]. For eliminations there is evidence that a change in the leaving group basicity is accompanied by a change of the value of k_H/k_D, the ratio decreasing in the order Br > OTs > $^+S(CH_3)_2$

$>^+N(CH_3)_3$ [7]. This corresponds to a shift of the transition state from the central structure (bromides) to a more carbanion-like one (ammonium salts). Less definite is the interpretation of the data when the basicity is changed. Cockerill found [17] that, for 2-phenylethyl dimethylsulphonium bromides, k_H/k_D increased to a maximum and then decreased again when the basicity, and hence the rate, was greatly enhanced. His conclusions are that the transition state structure changes to a more reactant-like transition state by a gradual reduction in the extent of proton transfer. Finally, there were no data available until very recently* concerning the variation of k_H/k_D with the acidity of the α-hydrogens. In a recent review Fry [18] has suggested that deuterium isotope effect should decrease regularly, or perhaps increase to a maximum and then decrease, by changing the substituent in the phenyl ring from p-OCH_3 to p-NO_2. We have measured the kinetic isotope effect for both bromides and tosylates in ethanol and in t-butanol and the values are reported in Tables 1 and 2. The free, the complexed and the p-nitro substituted arene were chosen in the expectation that k_H/k_D would change because of the probable variation of transition state geometry. No correction has been applied for a secondary isotope effect due to the presence of the second deuterium atom which, however, should be very small, and of a quantum mechanical tunnelling effect which should account for some values higher than those calculated [16]. The presence of a proton tunnelling effect cannot be completely excluded even though Blackwell's recent results on elimination of 2-phenylethyl bromides [19] have shown that tunnelling is an important factor in the elimination of 2-phenylethyl bromides when electron-releasing substituents are present (p-OCH_3), but it is of minor importance when electron withdrawing groups (p-NO_2) are in the ring.

For 2-phenylethyl bromides, it appears that there is a common trend of k_H/k_D both in ethanol and in t-butanol, i.e. k_H/k_D increases with the electron withdrawing power of the substituent, *although the extent of the effect is so small that in some cases it is within the limits of experimental error.* Thus, there is no evidence for the existence of a maximum by changing the acidity of the α-hydrogens, at least with bromide as leaving group. The data obtained by Blackwell at 30° on the series of substituted 2-phenylethyl bromides in the same solvent/base system (k_H/k_D = 8.12 for the parent compound, 9.14 for the p-nitro) confirm that the isotope effect increases very smoothly with the electron withdrawing effect of substituent. In the hypothesis that the small increase observed is real, this would indicate that the transition state geometry is shifted towards a more carbanion-like character. However, the proton should be less than half transferred to the base at the transition state (rising arm of the curve k_H/k_D vs. C—H stretching).

The data for tosylates are slightly different. While in ethanol there is a small increase, k_H/k_D shows a maximum corresponding to the chromium tricarbonyl substrate in tert-butanol (Table 2). As tosylates utilize transition state structures more carbanion-like than bromides especially in t-butanol, by increasing the acidifying character of the substituent one shifts the geometry of

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* While this manuscript was in progress, a paper appeared by F.L. Blackwell et al. [19] who measured k_H/k_D for a series of substituted phenylethyl bromides in t-butyl alcohol with potassium t-butoxide. His data and conclusions are very similar to ours and will be referred to in the course of the discussion.

the transition state towards structures where the proton is half or more than half transferred to the base (*p*-nitro should be on the descending arm of the curve).

Whether the trend observed and the maximum appear real or not, it seems clear that the shape of the curve is rather flat and k_H/k_D is a very "poor" probe in order to investigate the detailed geometry of the transition state; alternatively it may be that the symmetry of the transition state does not change over the range of substituents examined.

In conclusion, the isotope effect data, together with the nature and proportions of the products and the solvent/base effect, indicate that chromium tricarbonyl substrates react in elimination reactions through a transition state structure which fits very well into the spectrum proposed for the uncomplexed substrates. The unique effect of the metal group is to increase appreciably the yield of olefin and the rate of elimination.

Experimental

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

(2-Phenylethanol)chromium tricarbonyl, (2-phenylethyl *p*-toluenesulfonate)chromium tricarbonyl and (2-phenylethyl bromide) chromium tricarbonyl have been described previously [8].

2-Phenyl-2,2-d_2-ethanol

The alcohol was obtained by reduction of 2-phenyl-2,2-d_2-acetic acid with $LiAlH_4$ in ether. The deuterated acid was obtained by refluxing a solution of the sodium salt in basic deuterium oxide, following the method described by J.G. Atkinson [20]. The extent of deuteration determined by NMR was > 99 atom % D. The deuterated 2-phenylethyl tosylate and bromide (parent, complexed and *p*-nitro substituted) have been obtained from the alcohol by usual procedures. Physical properties and spectroscopic characteristics were in agreement with their structure.

(1-Phenyl-2-propyl p-toluenesulphonate)chromium tricarbonyl

The complex was made from the complexed 1-phenyl-2-propanol and *p*-toluenesulphonyl chloride in pyridine at —10°. The complexed alcohol was obtained by heating hexacarbonylchromium with the alcohol following the usual procedure. Crystallization from benzene/light petroleum gave a yellow product, m.p. 131°. (Found: C, 53.51; H, 4.31; S, 7.28. $C_{19}H_{18}CrO_6S$ calcd.: C, 53.51; H, 4.25; S, 7.51%.)

IR and NMR analyses were consistent with the structure.

(1-Phenyl-2-propyl bromide)chromium tricarbonyl

(1-Phenyl-2-propyl-OTs)chromium tricarbonyl (10^{-2} moles) and 4×10^{-2} moles of LiBr were dissolved in acetone previously deaerated with N_2. The solution was kept in the dark for 24 h. Recrystallization from ether/light petroleum gave the product. Yield 80%, m.p. 80—81°. (Found: C, 43.02; H, 3.30; $C_{12}H_{11}BrCrO_3$ calcd.: C, 43.00; H, 3.31%.)

Kinetic measurements

Anhydrous ethanol was prepared by the method of Lund [21] and t-butyl alcohol was purified as described by Cockerill [22]. Standard solutions of alkoxide were obtained by dissolving the clean metal in the alcohol and standardization was performed just before use using 0.1 *M* hydrochloric acid and phenolphthalein indicator. Fresh base solutions were prepared at least every four days.

Two cuvettes were filled with the alkoxide solutions (2.5 cm^3) and placed in the thermostatted cell compartment of a Unicam SP 800 or of a Cary model 14 spectrophotometer. After thermal equilibrium has been achieved, 250 λ of the substrate solution was introduced from a microsyringe into one of the cuvettes. The cell was rapidly shaken and the percentage transmission monitored as a function of time. The base was in large excess so that pseudo-first-order kinetics were observed. The appearance of styrenes was followed at 260 nm for the parent, at 302 nm for the *p*-nitro and at 413 nm for the complexed substrates. The infinity transmission was read after 8—10 half-lives of the reaction. Styrenechromium tricarbonyl was prepared by the method of Rausch [23] and the mixture of (1-phenyl-1-propene and 3-phenyl-1-propene)-chromium tricarbonyl by reaction of 1-phenyl-2-propyl tosylate with $Cr(CO)_6$ in n-butyl ether (see below). The infinity UV spectra of reaction solutions were identical to the spectra of solutions prepared from authentic samples.

Product analysis

The products and their percentages were determined by GLC analysis and comparison with authentic samples. Samples of the olefins were obtained by dissolving the substrates (0.5 g) in alcohol with the appropriate base and allowing reaction to proceed for 10 and 20 half-lives. After normal work-up the olefins were isolated. With complexed substrates the yellow extract (pentane) was treated with 10 ml of freshly prepared ceric ammonium nitrate in acetone [5]. After 10 min of stirring, the solution was washed with portions of cold water, dried over $MgSO_4$, reduced to a small volume and then analyzed for olefins.

Reaction between 1-phenyl-2-propyl tosylate and $Cr(CO)_6$

To 60 ml of n-butyl ether freshly distilled from sodium and 10 ml of heptane was added 0.020 mol of the tosylate and 0.023 mol of chromium hexacarbonyl. The mixture was heated in the dark in the apparatus described by Strohmeier [24] until no more hexacarbonyl sublimed. After cooling, the solvent was distilled off under reduced pressure, the residue diluted with ether and filtered through deactivated alumina. After removal of the solvent the residue was analyzed. Thin layer chromatography showed the presence of at least three products which were separated by column chromatography (silica gel, eluent benzene/light petroleum 1/2 v/v): uncomplexed and complexed tosylates (very small amounts) and a yellow oil which analysis by NMR, IR and UV showed to be a mixture of (1-phenyl-1-propene)chromium tricarbonyl and (3-phenyl-1-propene)chromium tricarbonyl. The mixture was subjected to oxidative decomplexation by ceric ammonium nitrate and analyzed by GLC on the 7' SE 30 column. Of the three peaks, whose relative retention times and areas were: 4.4, 6.1, 8.1; 6%, 18%, 76%, respectively, the first peak had a retention time under the same conditions identical with that of authentic 3-phenyl-1-propene; the second peak with that of *cis*-1-phenyl-1-propene and the third peak with that of *trans*-1-phenyl-1-propene.

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