Journal of Organometallic Chemistry, 72 (1974) 189—195

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

V*. ELIMINATION FROM (1-PHENYL-1-CHLOROPROPANE)-, (1-PHENYL-2-PROPYL BROMIDE)- AND (1-PHENYL-2-PROPYL TOSYLATE)-CHROMIUM TRICARBONYL INDUCED BY HALIDE IONS IN ACETONE

A. CECCON

Istituto di Chimica Fisica, Università di Padova, 35100 Padova (Italy)

(Received November 19th, 1973)

Summary

Rate constants are reported for the second-order elimination reactions of $Ph(Cl)CHCH_2CH_3$, $PhCH_2C(OTs)HCH_3$ and $PhCH_2C(Br)HCH_3$, alone and complexed with $Cr(CO)_3$, induced by $n\text{-}Bu_4NCl$ and $n\text{-}Bu_4NBr$ in acetone. Complexation does not appreciably affect the rate of dehydrochlorination of 1-phenyl-1-chloropropane but decreases the olefin yield and the rate of elimination for the 1-phenyl-2-propyl derivatives. It is considered that an *E2C* transition state explains the observed effects better than an *E2H* one.

Introduction

Reactions at the α-carbon** atom of the side chain of an arene whose transition state has a well-pronounced carbonium ion or carbanion character are strongly accelerated when the phenyl ring is complexed with the $Cr(CO)_3$ group [1, 2]. Even though the mechanisms through which the effects take place are subject to controversy [3, 4], the size of the effect on the rate, which is of the order of 10^4-10^5 for carbonium ion-like and 10^2 for carbanion-like reactions, cannot be questioned. On the basis of these huge effects, chromium tricarbonyl might be used as a "probe" to test the transition state structure of side-chain reactions occurring at the α-carbon.

In Part IV of this series we have examined the kinetic influence of complexation on the elimination from 2-phenylethyl and 1-phenyl-2-propyl bromides

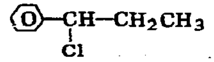
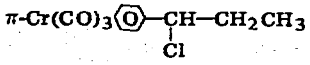
---

[*] For Part IV see ref. 1.

[**] α refers to the carbon adjacent to the phenyl ring and β to the more remote one, irrespective of the position of the leaving group.

TABLE 1

RATES OF SOLVOLYSIS, (k_s), AND ELIMINATION, (k_{el}), OF COMPLEXED AND UNCOMPLEXED 1-PHENYL-1-CHLOROPROPANE IN ACETONE AT 75°

Substrate [a]	Salt	$k_s \times 10^7$ (sec^{-1})	$k_{el} \times 10^5$ [b] (l·mol^{-1}·sec^{-1})
 $\langle\mathrm{O}\rangle-\underset{\underset{\mathrm{Cl}}{\vert}}{\mathrm{C}}\mathrm{H}-\mathrm{CH_2CH_3}$	$(n\text{-}Bu)_4NClO_4$	0.08	
	$(n\text{-}Bu)_4NCl$		1.0
 $\pi\text{-}\mathrm{Cr(CO)_3}\langle\mathrm{O}\rangle-\underset{\underset{\mathrm{Cl}}{\vert}}{\mathrm{C}}\mathrm{H}-\mathrm{CH_2CH_3}$	$(n\text{-}Bu)_4NClO_4$	32.4	
	$(n\text{-}Bu)_4NCl$		0.6

[a] Concentration of reactants: substrate, 0.05 *M*; salt, 0.07-0.1 *M*. Values of rate constants are measured at the same ionic strength. 2,6-Lutidine, 0.055 *M*. [b] Reaction products: *trans*-1-aryl-1-propene 99%; *cis*-1-aryl-1-propene 1%.

and tosylates in alcohols catalyzed by metal alkoxides. Under these conditions, the transition state character varies from central to paenecarbanion (*E*1*cb*-like) in the spectrum of structures *E2H** according to the nature of the leaving group, solvent-base system and substituents; complexation increases the rate of elimination by a factor which varies from 10 to 500 depending mainly on leaving group (bromide or tosylate) and on solvent.

It is known that secondary and tertiary halides and sulphonate esters can undergo olefin-forming eliminations without necessarily requiring the presence of a strong base [5]. For example, acetone with tetrabutylammonium chloride has been shown to be often even more effective in promoting the elimination than the alcoholic media. Under these conditions, i.e. dipolar aprotic solvents in the presence of a catalyst which is a very poor base but a strong nucleophile, the transition state structure is characterized by: (*a*) well developed double bond character, (*b*) little or no positive charge at the atom carrying the leaving group, (*c*) little or no negative charge at the carbon from which the proton is abstracted, (*d*) some interaction of the base with the atom carrying the leaving group (*E2C* transition state) [5]. Some authors have questioned this picture, especially the existence of some kind of interaction of the nucleophile with carbon [6]. They claim that the transition state for reactions in dipolar aprotic solvents still belongs to the *E2H* spectrum; secondary and tertiary derivatives would utilize transition-state structures from central to the E_1-like extreme of the spectrum. According to this interpretation the carbon to which the leaving group is attached should be partially positively charged.

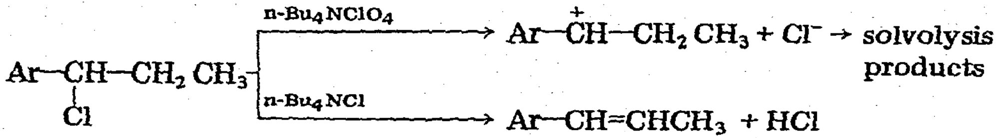
The results of the effects promoted by the $Cr(CO)_3$ on the rate of reactions with charged transition states [1, 2b, c] prompted us to investigate the effect of complexation on the elimination from secondary halides and tosylates induced by halide ions in acetone.

Results and discussion

The rates of solvolysis, k_s, and dehydrochlorination with 0.1 *M* n-Bu_4NCl, k_{el}, of 1-phenyl-1-chloropropane, free and coordinated with $Cr(CO)_3$, in acetone containing 2,6-lutidine at 75° are reported in Table 1.

---

* *E2H* and *E2C*, as classified by Parker and Winstein [5], are the eliminations (and transition state structures) occurring in alcoholic media with strong bases and in dipolar aprotic solvents with strong nucleophiles, respectively.



$$Ar{-}\underset{Cl}{CH}{-}CH_2CH_3 \begin{cases} \xrightarrow{n\text{-}Bu_4NClO_4} Ar{-}\overset{+}{C}H{-}CH_2CH_3 + Cl^- \rightarrow \text{solvolysis products} \\ \xrightarrow{n\text{-}Bu_4NCl} Ar{-}CH{=}CHCH_3 + HCl \end{cases}$$

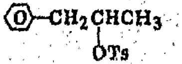
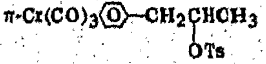
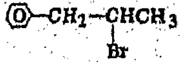
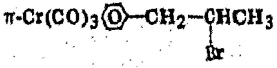
Unimolecular elimination $E1$ as measured by the rate of acid production in 0.1 M n-Bu_4NClO_4 is extremely sensitive to complexation of the ring with the metal group. While for the uncomplexed compound the rate is so slow that only an upper limit could be determined, the complexed chloride reacts reasonably rapidly. The value of the ratio $k_{s[Cr(CO)_3]}/k_{s[H]} > 400$ can be explained by the extraordinary capacity of the chromium tricarbonyl group to stabilize an α-carbonium ion-like transition state, if one considers that the effect on secondary systems should be lower than that observed on primary benzyl chlorides (10^4 - 10^5) [2a].

In contrast, the rate of dehydrochlorination catalyzed by tetrabutylammonium chloride, k_{e1}, is essentially unaffected by complexation (see Table 1). The second-order rate constant for the complexed substrate is inaccurate because solvolysis, which is only a minor fraction of the overall reaction for the uncomplexed chloride in the presence of 0.1 M tetrabutylammonium chloride, comprises almost all the reaction for the complexed chloride under the same conditions. The second-order rate constant is obtained from the small difference between the observed rate constant and the rate of solvolysis measured at the same ionic strength and is, therefore, subject to large errors. In spite of this uncertainty, it is clear that the presence of the nucleophile Cl^- is necessary for elimination in the parent chloride whereas it has no catalytic action and the same "normal" salt effect as tetrabutylammonium perchlorate in the reaction with the complexed chloride. Thus, on the basis of the large accelerating effect promoted by $Cr(CO)_3$ on the unimolecular elimination, one would expect a similar, though lower, effect on the halide promoted elimination if a carbonium ion-like transition state were utilized. The absence of any accelerating effect indicates that the α-carbon, which in this case carries the leaving group, possesses no positive charge in the transition state for elimination indicating an $E2C$ mechanism with a well developed double bond between C_α and C_β.

The results for 1-phenyl-2-propyl derivatives (Table 2) compared with those obtained on the same substrates in alcoholic media [1] show the radically different effects caused by chromium tricarbonyl in $E2H$ and $E2C$ eliminations. The % elimination, F_E, of 1-phenyl-2-propyl tosylate increases from 90 to 100% on complexation in ethanol with sodium ethoxide [1]; in acetone with chloride ion F_E is reduced from 8.7 to 0.5%. Even more significant are the data on rates [for 1-phenyl-2-propyl tosylate and bromide unimolecular solvolysis does not compete with bimolecular elimination and substitution; it seems that there is no appreciable stabilization of the β-carbonium ion by $Cr(CO)_3$]: in ethanol with sodium ethoxide and in tert-butanol with potassium tert-butoxide the accelerating effect of chromium tricarbonyl on the rate of base catalyzed reaction of tosylate is 49 and 276 respectively [1]. In acetone the effect is in the oppo-

TABLE 2

RATES AND PRODUCTS OF ELIMINATION FROM COMPLEXED AND UNCOMPLEXED 1-PHENYL-2-PROPYL TOSYLATES AND BROMIDES IN ACETONE AT 75° CATALYZED BY HALIDE IONS

Substrate [a]	Salt	$F_E \times 10^2$ [b]	$k_{el} \times 10^4$ [c,e] ($l \cdot mol^{-1} \cdot sec^{-1}$)	$k_{sub} \times 10^2$ [c,e] ($l \cdot mol^{-1} \cdot sec^{-1}$)	Olefins [d] (%)		
					1-Aryl-1-propene		3-Aryl-1-propene
					cis	*trans*	
 $C_6H_5\text{–}CH_2CH(OTs)CH_3$	$(n\text{-}Bu)_4NCl$	8.7	10.4	1.11	23	71.5	5.5
 $\pi\text{-}Cr(CO)_3C_6H_5\text{–}CH_2CH(OTs)CH_3$		0.5		5.45			
 $C_6H_5\text{–}CH_2\text{–}CH(Br)CH_3$	$(n\text{-}Bu)_4NBr$	100	0.42 [c]		8.2	90.4	1.4
 $\pi\text{-}Cr(CO)_3C_6H_5\text{–}CH_2\text{–}CH(Br)CH_3$		100	0.09		8.0	80.0	12.0

[a] Concentration of reactants: substrate, 0.04—0.05 *M*; base 0.1 *M*; 2,6-lutidine 0.055 *M*. [b] F_E is the fraction of acid produced to chloride or bromide ion consumed + acid generated. [c] Estimated from total rate and F_E. [d] Percentage of the total olefins. [e] Biale et al. [5c] reported for uncomplexed substrates values for F_E, k_s and k_{el} which are very close to those reported by us.

site direction and the elimination is so decreased on complexation that the only reaction observed is the bimolecular substitution to give the corresponding chloride. Moreover, the rate of elimination of 1-phenyl-2-propyl bromide, which represents the only reaction when the catalyst is the bromide ion, is diminished by $Cr(CO)_3$ by a factor of 5, $k_{\mathrm{el}\,Cr(CO)_3}/k_{\mathrm{el}(H)} = 0.21$.

We have attributed the accelerating effect observed in the alcohols to the strong inductive electron-withdrawing power of the phenylchromium tricarbonyl moiety which is much more effective than the phenyl ring in stabilizing an α-carbanion-like transition state (*E*1*cb*-like) [1]. The absence of such an effect in acetone clearly suggests that no fraction of negative charge is present at C_α. It is worth noticing that the electron-attracting power of the group is still operating in acetone. In the reaction of chloride ion with the sulphonate ester, in fact, the rate of substitution increases on complexation by a factor of 5, from 1.11×10^{-2} to 5.45×10^{-2}. The effect is similar to that measured for the substitution of 2-phenylethyl bromide by thiocyanate ion in the same solvent, which was shown to be equivalent to that of a *p*-nitro group [7]. Therefore, the preferential stabilization of the transition state for substitution (which carries a very small negative charge at C_β) excludes any possibility that C_α (which is closer to the ring) has an even smaller fraction of negative charge, in agreement with an *E*2*C* transition state picture.

The retarding effect of the bulky chromium tricarbonyl on k_{el} could be explained in terms of steric hindrance to the approaching base or inhibited solvation of the leaving group. However, our previous results for elimination with the same substrates in alcoholic media exclude a predominant role for such an effect in *E*2*H* conditions, even for bulky bases such as tert-butoxide. On the other hand, we have shown [7] that the β-carbon atom is too remote from the metal group for steric factors to predominate in bimolecular substitutions. The interaction between the nucleophile and the β-carbon suggested by Parker and Winstein [5] for the *E*2*C* transition state is loose, and certainly less tight than that in S_N2 reactions. Consequently no steric retardation is expected for *E*2*C* eliminations. The decrease in rate can plausibly be associated with the lower capacity of phenylchromium tricarbonyl compared with phenyl to conjugate with the well-developed double bond at the transition state. As Parker and Winstein pointed out, phenyl substituents are bulky and they conjugate with double bonds only if they can achieve coplanarity, suggesting that the relatively negligible effect of aryl groups in stabilizing *E*2*C* transition states could be attributed to little conjugation with the phenyl ring. One does not expect better stabilization by the more bulky phenylchromium tricarbonyl substituent. Some support for this interpretation comes from the data for product distribution, in alcohols and in acetone. In ethanol and in tert-butanol the large accelerating effect of complexation does not significantly alter the relative proportions of the olefin isomers. (Hoffman/Saytzeff ratio) [1]. In acetone the yield of Hoffman product, 3-phenyl-1-propene, increases from 1.4 to 12 per cent on passing from phenyl to phenyl $Cr(CO)_3$ (Table 2). The higher proportion of unconjugated olefin confirms that the phenylchromium tricarbonyl group is unable to conjugate with double bonds, and so to stabilize the very product-like *E*2*C* transition state.

Experimental

Materials

Acetone was dried, 2,6-lutidine purified, and dry n-Bu_4NCl and n-Bu_4NBr prepared according to standard procedures. 1-Phenyl-1-chloropropane, 1-phenyl-2-propyl tosylate and bromide were obtained from the corresponding alcohols in the usual way. The physical and spectroscopic characteristics were in accord with their structures and published data.

(1-Phenyl-2-propyl *p*-toluenesulphonate)chromium tricarbonyl and (1-phenyl-2-propyl bromide)chromium tricarbonyl have been previously described [1].

(1-Phenyl-1-chloropropane)chromium tricarbonyl

The chloride was prepared from the corresponding complexed alcohol in ether by bubbling anhydrous HCl at 0° in the presence of $CaCl_2$. The product is an air sensitive orange-yellow oil. NMR analysis showed the presence, besides that of the complexed chloride [δ 5.29 ppm π-$Cr(CO)_3C_6H_5$] of a certain amount of uncomplexed compound (δ 7.35 ppm C_6H_5). From NMR, GLC and elemental analysis it was calculated that 7 per cent of the 1-phenyl-1-chloropropane was present in the mixture. No purification by column chromatography was attempted because of the instability of the product, which was used as such for the kinetics. Reactant concentrations and rate constants were calculated by considering the effective concentration of complexed chloride.

Kinetic measurements

Runs were carried out using the sealed ampoules technique; a stream of presaturated nitrogen was bubbled through for the complexed compounds. Acid was determined by pouring the sample in pyridine and quickly titrating with sodium methoxide in methanol, using Thymol Blue as indicator. For reactions with n-Bu_4NCl a second sample was poured into pentane and extracted with water; the aqueous extracts were titrated for chloride ion by the Volhard method. Rate coefficients $k_{el} + k_{sub}$ for the total reaction were obtained by adding the observed rates of chloride ion consumption and acid production. Product analyses and some runs of 1-phenyl-1-chloropropane were determined by GLC.

Acknowledgements

This work was supported in part by the National Research Council of Italy, through its "Centro Studi sugli Stati Molecolari Radicalici ed Eccitati".

References

1 A. Ceccon and G. Catelani, J. Organometal. Chem., 72 (1974) 179.
2 (a) J.D. Holmes, D.A.K. Jones and R. Pettit, J. Organometal. Chem., 4 (1965) 324;
(b) A. Ceccon, J. Organometal. Chem., 29 (1971) C19;
(c) A. Ceccon and G.S. Biserni, J. Organometal. Chem., 39 (1972) 313.
3 E.A. Hill and S.H. Richards, J. Amer. Chem. Soc., 81 (1959) 3483; 83 (1961) 3840, 4216. J.C. Ware, and T.G. Traylor, Tetrahedron Lett., 18 (1963) 1295; J. Amer. Chem. Soc., 89 (1967) 2304; W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 829; J. Amer. Chem. Soc., 92 (1970) 7476; R.E. Davis, H.D. Simpson, N. Grice and R. Pettit, J. Amer. Chem. Soc., 93 (1971) 6688.
4 D.A. Brown, J. Chem. Soc., (1963) 4389; G. Klopman and K. Noak, Inorg. Chem., 7 (1968) 579; S.P. Gubin and V.S. Khandkarova, J. Organometal. Chem., 22 (1970) 449.

5 (a) S. Winstein, Chimica Teorica, Accad. Nazionale Lincei, Roma (1965);
(b) G. Biale, A.J. Parker, S.G. Smith, I.D.R. Stevens and S. Winstein, J. Amer. Chem. Soc., 92 (1970) 115;
(c) G. Biale, D. Cook, D.J. Lloyd, A.J. Parker, I.D.R. Stevens, J. Takanashi and S. Winstein, J. Amer. Chem. Soc., 93 (1971) 4735;
(d) D.J. Lloyd and A.J. Parker, Tetrahedron Lett., (1970) 5029;
(e) A.J. Parker, M. Ruane, D.A. Palmer and S. Winstein, J. Amer. Chem. Soc., 94 (1972) 2228;
(f) G. Biale, A.J. Parker, I.D.R. Stevens, J. Takahashi and S. Winstein, J. Amer. Chem. Soc., 94 (1972) 2235;
(g) P. Beltrame, G. Biale, D.J. Lloyd, A.J. Parker, M. Ruane and S. Winstein, J. Amer. Chem. Soc., 94 (1972) 2240;
(h) P. Beltrame, A. Ceccon and S. Winstein, J. Amer. Chem. Soc., 94 (1972) 2315.
6 J.F. Bunnett, Survey Prog. Chem., 5 (1969) 53; J.F. Bunnett and E. Baciocchi, J. Org. Chem., 32 (1967) 11; D. Eck and J.F. Bunnett, J. Amer. Chem. Soc., 91 (1969) 3099; O.R. Jackson, D.J. McLennan, A.S. Short and R.J. Wong, J. Chem. Soc., Perkin Trans. II, (1972) 2308.
7 A. Ceccon and S. Sartori, J. Organometal. Chem., 50 (1973) 161.