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Reactions of organic anions

CLXII *. Why do η^6-arenetricarbonylchromium(0) π-complexes not enter the vicarious nucleophilic substitution of hydrogen?

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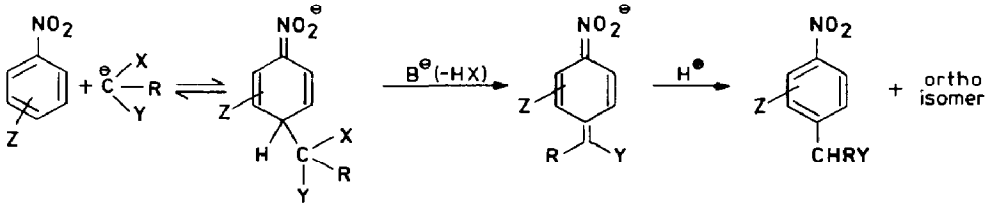
Abstract

Attempts to perform the vicarious nucleophilic substitution of hydrogen in highly electrophilic η^6-arenetricarbonylchromium(0) π-complexes failed. Reasons for this unexpected failure are discussed.

Introduction

The vicarious nucleophilic substitution of hydrogen (VNS) is a reaction between carbanions bearing leaving groups X at the carbanionic center and electrophilic aromatic compounds. It proceeds via addition of the carbanionic species to the aromatic ring to give anionic σ-adducts, which undergo base induced β-elimination of HX. The final products are obtained upon protonation. This reaction has been successfully developed for various aromatic nitro compounds [2].



X-leaving group, Y-stabilizing group, R-substituent

In recent years it has been shown that the VNS reaction proceeds efficiently with many electrophilic aromatic compounds which do not contain a nitro group:

* For part CLXI see ref. 1.

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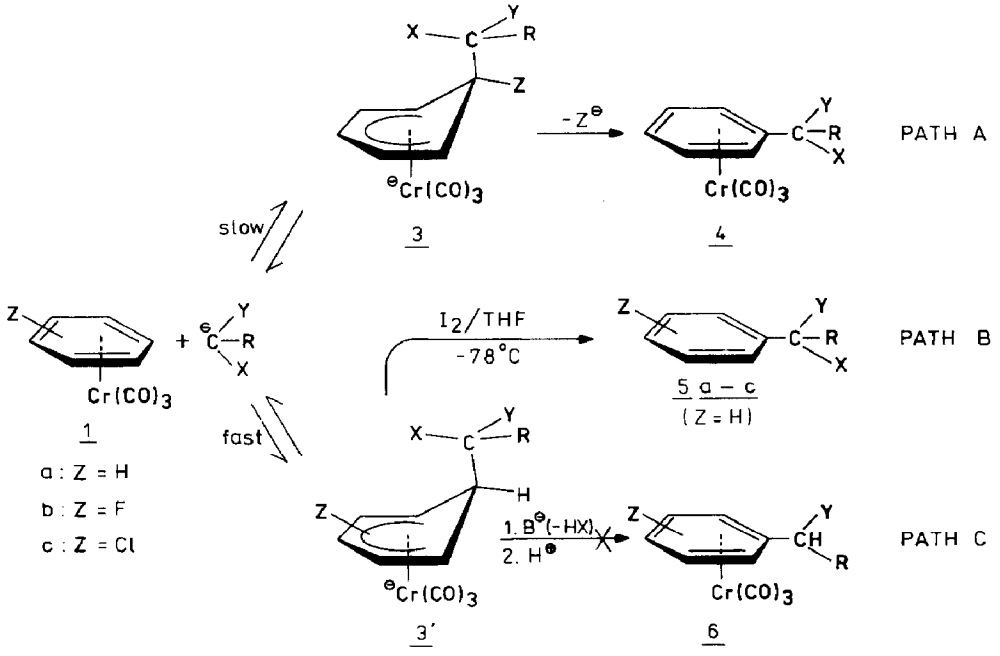
heterocycles [3a–c], cyanonaphthalenes [4], quinones [5] and tropylium salts [6]. Thus,it can be considered as an efficient and general method for the introduction of α-functionalized substituents into electrophilic aromatic rings.

On the other hand aromatic compounds complexed with a tricarbonylchromium group exhibit high electrophilicity and enter a variety of reactions with nucleophilic agents, particularly carbanions [7]. Therefore, we have attempted to perform vicarious nucleophilic substitution with these compounds.

Results and discussion

Carbanions possessing high nucleophilicity react with arenechromium π-complexes to form quantitatively the corresponding anionic σ(H)-adducts (3′). Addition to carbon atoms connected with hydrogen is usually faster than to those connected with nucleofugal groups Z (Z = halogen, methoxy, etc.). In this respect there is a strong similarity of these reactions to those with nitroarenes. Oxidation of the σ(H)-adducts (3′) (path B) leads to the final products of oxidative nucleophilic substitution of hydrogen in aromatic rings (5).

Less nucleophilic carbanions also form σ(H)-adducts, but equilibrium constants are substantially lower, so the oxidation of the σ(H)-adducts is no longer feasible since starting π-complexes (1) and the corresponding carbanions, existing in the solution in high concentrations, are also very susceptible to oxidation. However, in these cases in the absence of oxidant typical nucleophilic substitution of nucleofugal groups Z still occurs easily (path A), even with carbanions of moderate nucleophilicity (e.g. $^{-}CH(CO_2Et)_2$) [7a].



The metal coordinated with the aromatic ring exerts powerful electron-withdrawing effect, apparently stronger than does a nitro substituent in the σ bond framework, and the corresponding arene π-complexes behave in reactions with nucleophiles similarly to electrophilic nitroarenes. We therefore expected that they should enter the VNS reaction in an analogous way to the nitro compounds.

Since attempts to carry out the reaction of benzene-tricarbonylchromium(0) with chloromethyl aryl sulfones, which are standard CH acids for the VNS reaction, were unsuccessful, we have tried to perform the VNS using various combinations of carbanions with procedures and reaction conditions appropriate for this reaction [2] (an excess of base has been always used). All of these experiments failed; upon protonation of the reaction mixtures starting materials were usually recovered.

These completely negative results can be explained by insufficient addition equilibrium or difficulties in the elimination step. To clarify this question, namely to discover at which step the VNS process in benzene-tricarbonylchromium(0) π-complexes is hindered, we have carried out several experiments using highly nucleophilic carbanions of: thioanisole ($^-CH_2SPh$), benzyl phenyl sulfide ($^-CH(SPh)Ph$) and benzyl phenyl surfone ($^-CH(SO_2Ph)Ph$), bearing leaving groups and having the potential to enter the VNS (with nitroarenes, $^-CH(SPh)Ph$ readily effects the VNS [14]). In these cases the VNS has not occurred, but treatment of the reaction mixture with iodine resulted in the formation of the corresponding products of oxidative replacement of hydrogen (path B). These results confirm without doubt that the σ(H)-adducts are formed and that the addition equilibrium constants are sufficiently high. On the other hand the oxidative replacement of hydrogen in the benzene-chromium(0) π-complex did not occur with less nucleophilic carbanions ($^-CH(Cl)SO_2Ar$, $^-CH(OPh)CN$, $^-CH(SAr)CN$, $^-CCl(CH_3)CN$), which are very efficient in the VNS in nitroarenes. Apparently the equilibrium constants of the addition of these carbanions to arene π-complexes are small, similar to those reported in literature for reaction of malonate anion [7a].

For these carbanions also, the VNS reaction in π-complexes was not observed. In order to check whether such carbanions add to the benzene-tricarbonylchromium(0) π-complexes at all, the anion of chloromethyl *para*-tolyl sulfone was subjected to the reaction with η^6-fluoro- and chloro-benzene tricarbonylchromium(0) (**1b**, **1c**). In these reactions the nucleophilic replacement of halogen by the carbanion took place, which is evidence for formation of σ(Z)-adducts, **3** (path A). It is well documented, that the formation of σ(H)-adducts (from which the β-elimination of HX was expected in the VNS reaction) occurs faster that the formation of σ(Z)-adducts. Thus, these results imply that σ(H)-adducts of our selected carbanion ($^-CH(Cl)SO_2Tol$) to arene-chromium π-complexes are formed and probably all of the carbanions tested form such type of adducts (**3'**). So, an absence of the vicarious nucleophilic substitution of hydrogen in η^6-arenetricarbonylchromium(0) π-complexes (path C) must be caused by difficulties in the elimination step.

The answer to the question posed in the title is drawn from a detailed inspection of the structure * of σ(H)-adduct (Fig. 1).

(1) In the elimination process a base (BuLi, LDA, t-BuOK) should abstract the *endo* hydrogen. The approach of base, bearing a negative charge, to this hydrogen

* This structure is drawn on the basis of X-ray data [8].

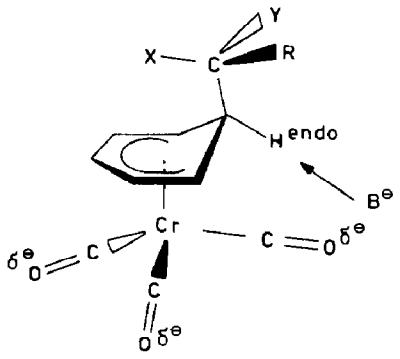


Fig. 1.

Table 1

Reactions of η^6-arene-tricarbonylchromium(0) π-complexes with carbanions bearing leaving groups

Complex	Carbanion			Pathway	Product	Yield (%)
	R	Y	X			
1a	H	H	SPh	B	**5a**	43
1a	H	Ph	SPh	B	**5b**	52
1a	H	Ph	SO_2Ph	B	**5c**	51
1b	H	Ts	Cl	A	4	46
1c	H	Ts	Cl	A	4	12

atom is hindered because of its electrostatic repulsion by the negatively charged carbonyl groups.

(2) The β-elimination of HX requires an antiperiplanar arrangement of H^{endo} and a leaving group X as shown in Fig. 1. This conformation is unfavorable, because of the steric interaction of the leaving group with the cyclohexadienyl system. Additionally, departure of the leaving group X in the anionic form can also be hindered by π electrons of the complexed six-membered ring.

(3) Steric interactions of the base with the bulky $Cr(CO)_3$ unit are also possible (similarly steric hindrance was observed earlier in catalytic aminodefluorination reactions of η^6-fluorobenzene-tricarbonylchromium(0) [15]).

Thus, we can conclude that η^6-arene-tricarbonylchromium(0) π-complexes, in spite of high electrophilicity, do not enter the vicarious nucleophilic substitution of hydrogen due to severe difficulties in β-elimination from the σ(H)-adducts of carbanions.

Experimental

η^6-Arene-tricarbonylchromium(0) π-complexes were prepared by procedures given in the literature [9,10]. Other starting materials were commercially available or prepared according to standard procedures. All addition-oxidation reactions were carried out in the usual ways [7a,11]. Products were purified by column chromatography (n-hexane: chloroform mixture; silica gel 200–300 mesh, Merck) and identified on the basis of ^1H NMR spectra (usually Varian EM-360, 60 MHz, in $CDCl_3$

with TMS as internal standard and by comparison of melting points with those reported in the literature. TLC analyses were made on foil plates (Merck 60F 254). All melting points are uncorrected.

Substitution of halogen in η^6-halogenobenzene-tricarbonylchromium(0) π-complexes

In a three-necked flask (50 ml) t-BuOK (80 mg, 0.71 mmol) was placed (under argon) in THF (5 ml). The solution was cooled to $-50\,^\circ$C and stirred. Then a solution of chloromethyl *p*-tolyl sulfone (146 mg, 0.71 mmol) in THF/HMPT (2/1; 1 ml) was added with a syringe. After 5 min π-complex of η^6-halogenobenzene-tricarbonylchromium(0) (**1b**, **1c**; 0.52 mmol) was added. The reaction was continued for a further 6 hours at room temperature. The mixture was poured into water (20 ml) and extracted with ether (2×10 ml). The combined organic layers were dried over $MgSO_4$. After evaporation of the solvent the crude product was purified via column chromatography (n-hexane/$CHCl_3$, 3/1). An analytical sample was recrystallized from n-hexane/ether (1/1) mixture (yellow crystals).

Products – properties and analyses

Benzyl phenyl sulfide (**5a**): m.p. 41–43°C (Et_2O), lit. [12], 43–44°C. ^{1}H NMR: 7.54–7.18 (m, 10H), 4.11 (s, 2H).

Benzhydryl phenyl sulfide (**5b**): oil, m.p. 78–79°C [12]. ^{1}H NMR: 7.70–7.07 (m, 15H), 5.63 (s, 1H).

Benzhydryl phenyl sulfone (**5c**): m.p. 192–193°C (EtOH), lit. [13], 187–88°C. ^{1}H NMR: 7.80–7.17 (m, 15H), 5.91 (s, 1H).

η^5-(α-Chloro-,α-*para*-tosyl)methylobenzene-tricarbonylchromium(0) [4]: M.p. (n-hexane/Et_2O) 160–162°C (decomp.). ^{1}H NMR (80 MHz): 7.80–7.20 (m, 4H, H-Tol), 5.65–5.05 (m, 6H, H–ArCr(CO)$_3$, CH), 2.46 (s, 3H, CH_3). MS (Finnigan 3200, *m/z*, % rel. int.): 246($M^{+\cdot}$ – Cr(CO)$_3$ – Cl$^\cdot$, 4), 242(1), 214(4), 139(3), 125(27), 105(11), 91(100), 84(5), 77(15), 64(16), 51(9), 40(14). Found: C, 48.55; H, 3.11. $C_{17}H_{13}ClCrO_5S$ calcd.: C, 48.99; H, 3.14%.

Acknowledgments

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