

REACTION OF CHLOROTOLUENETRICARBONYLCHROMIUM COMPLEXES WITH α -SULFONYL-CARBANIONS

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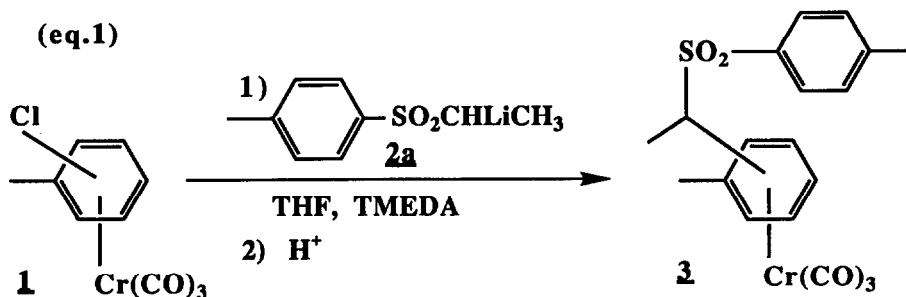
Abstract: Primary and secondary α -sulfonyl-carbanions react with chlorotoluenetricarbonylchromium complexes to give, after CF_3CO_2H treatment, aryl-sulfones via ipso, cine and tele nucleophilic aromatic substitution of chloride.

It is well known that stabilized carbon nucleophiles can react with arenetricarbonyl chromium complexes¹ to give anionic cyclohexadienyl intermediates, which in turn can yield substituted arenes² on oxidation and substituted cyclohexadienes on treatment with acids³ or electrophiles⁴ and with iodine. In either case, the tricarbonylchromium entity is lost. However, if the complex is substituted by a good leaving group, we recently described that cine and tele S_NAr occur without loss of the tricarbonylchromium entity⁵ if the complex is treated with a carbanion followed by an acid treatment.

The carbon nucleophiles which react with these complexes are very often stabilized carbanions such as α -alkoxycarbonyl, α -cyano, α -dithianyl, cyanohydrinacetal², α -amino-nitriles⁶ or esters^{6,7} carbanions. In some cases, alkyllithium can react with these complexes (e.g. $tBuLi$ ⁸) but other alkyllithium species fail because proton abstraction from the arene ligand becomes important². Anions less reactive than ester enolates² also fail, e.g. ketone enolates. We report here our first results relative to the reaction of chlorotoluenetricarbonylchromium complexes with a new type of anions: the α -sulfonylcarbanions.

P-toluenesulfonylethane carbanion **2a** (1.1 eq, obtained by lithiation of *p*-toluenesulfonylethane⁹ in THF at $-78^\circ C$ for 2 h and at $-10^\circ C$ for 10 mn) by treatment with *p*-chlorotoluenetricarbonylchromium complex **1a** in THF and TMEDA (1.1eq) ($-78^\circ C$, 1h; $-10^\circ C$, 30 mn; $0^\circ C$, 20 mn) yields after CF_3CO_2H treatment at $-78^\circ C$ disubstituted complexes

3a* (69% yield) and **3b*** (17% yield) (eq.1) (Table 1, entry 1). Similarly, carbanion **2a** reacts with *m*- and *o*-chlorotoluenetricarbonylchromium complexes **1b** and **1c** to give upon CF₃CO₂H treatment, respectively complexes **3a** (38% yield) and **3b** (38% yield) (Table 1, entry 2) and complex **3b** (81% yield) (Table 1, entry 3).



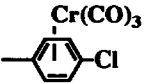
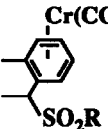
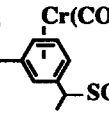
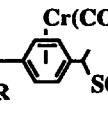
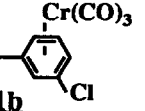
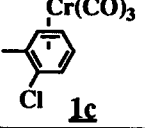
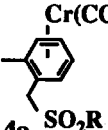
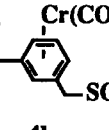
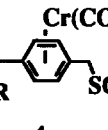
Primary carbanion** **2b**¹⁰ reacts similarly with complexes **1a**, **1b**, and **1c** to afford complexes **4** (Table 1, entries 4-8). It is worthy to note that complex **1a** and carbanion **2b** give the products **4a*** and **4b*** at -10°C (Table 1, entry 5) but only the complex **4b** under thermodynamic control¹¹ at 0°C (Table 1, entry 4). The same observation is made in the case of complex **1b** (Table 1, entries 6 and 7). In the case of *o*-chlorotoluene tricarbonylchromium, *p*-toluenesulfonylmethane carbanion yields after CF₃CO₂H treatment only the *meta*-disubstituted complex **4b** which is deuterated only at the C-2 position if CF₃CO₂D is used. These data prove definitively that a *cine* nucleophilic aromatic substitution occurs in this case and eliminates a possible *tele-para* S_NAr mechanism (Table 1, entry 8).

In conclusion, our results show that primary and secondary α-sulfonyl-carbanions react with chlorotoluenetricarbonylchromium complexes§ via *cine* and *tele*-S_NAr: this is to our knowledge without precedent in the literature and extends the number of nucleophiles able to react with these complexes. Carbanions **2a** and **2b** add to chlorobenzenetricarbonylchromium complexes via *ipso*, *cine* or *tele* S_NAr. In two cases, carbanion **2b** adds reversibly to these complexes even in the presence of one or two equivalents of TMEDA to give a regioselectivity which is not invariant in passing from kinetic to thermodynamic control. We shall describe this point in a near future.

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* Satisfactory spectral and analytical data have been obtained for all new compounds. NMR data CDCl₃: **3a**: -CHMe 1.54(d); ArMeCr 2.07(s); -C₆H₄-Me 2.43(s); -CHMe 3.85(q); ArH 5.02(d), 5.06(t), 5.19(d), 5.32(t); -C₆H₄- 7.29(d) and 7.55(d); **3b**: -CHMe 1.58(d); ArMeCr 2.14(s); -C₆H₄-Me 2.44(s); -CHMe 3.86(q); ArH 5.07(d), 5.08(s), 5.19(d), 5.21(t); -C₆H₄- 7.31 and 7.39ppm; **4a**: ArMeCr 2.05(s); -C₆H₄-Me 2.44(s); -CH₂- 4.23(d) and 3.80(d);

Table 1: Products obtained by treatment of halogenoarenetricarbonyl chromium complexes with α -sulfonyl carbanions ($R = -p\text{-C}_6\text{H}_4\text{CH}_3$)

Complex	Nucleophile ^k	Products (yield %)			Entry
 1a	2a $\text{RSO}_2\text{CHLiMe}$	 3a (69) ^f	 3b (17) ^e	 3c (0)	1^h 80/20/0
 1b	2a	(38) ^{e or g}	(38) ^{f or j}	(0)	2^h 50/50/0
 1c	2a	(0)	(81) ^e	(0)	3^h 0/100/0
1a	2b $\text{RSO}_2\text{CH}_2\text{Li}$	 4a (0)	 4b (72) ^e	 4c (0)	4^{a,j} 0/100/0
1a	2b	(20) ^f	(20) ^e	(0)	5^{b,i} 50/50/0
1b	2b	(9) ^{e or g}	(36) ^f	(12) ^e	6^{c,i} 16/63/21
1b	2b	(16) ^{e or j}	(27) ^{f or j}	(3) ^e	7^{d,i} 35/59/6
1c	2b	(3) ^f	(65) ^e	(0)	8^{c,i} 4/96/0

a: -10°C , 30mn; 0°C , 20mn (THF/TMEDA 1.1eq); b: -10°C , 150mn (THF/TMEDA 1.1eq) 50% of the starting material is recovered;
 c: 0°C , 20mn; d: -10°C , 10mn; e: cine SNAr; f: tele-meta SNAr;
 g: tele-para SNAr; h: ratio (3a/3b/3c); i: ratio (4a/4b/4c); j: ipso SNAr;
 k: in solution in THF in the presence of 1.1eq. of TMEDA

ArH: 5.38(t), 5.25(d), 5.14(m); **4b**: ArMeCr 2.13(s); -C6H4-Me 2.44(s); -CH2- 3.91(s); ArH 4.90(d), 4.99(s), 5.11(d), 5.36(t); -C6H4- 7.33(d) and 7.66(d); **4c**: ArMeCr 2.13(s); -C6H4-Me 2.44(s); -CH2- 3.85(s); ArH 5.11(d) and 5.22(d); -C6H4- 7.33(d) and 7.66(d).

** Tertiary carbanions of sulfones (e.g. *p*-toluenesulfonyl-2 butane) react with poor yields perhaps for steric reasons. Primary and secondary α -sulfonyl- carbanions do not react without TMEDA.

§ The same reactions work with trifluoromethylchlorobenzenetricarbonylchromium complexes but arenetricarbonylchromium complexes are contaminated by substituted cyclohexadienes because rearomatization does not occur systematically¹².

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