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REDUCTION OF NITRO- AND NITROSO-BENZENES TO AZOBENZENES PROMOTED BY TRIS(ACETONITRILE)TRICARBONYLCHROMIUM

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Summary

Treatment of various nitrobenzenes and nitrosobenzene with $(MeCN)_3Cr(CO)_3$ in refluxing cyclohexane affords low yields of the corresponding symmetrical azobenzenes

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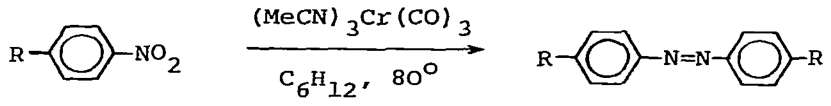
There have been several reports of the reduction of nitro-compounds in the presence of metal vapours [1] or organometallic complexes [2,3]; for example, anilines, azoxybenzenes, and azobenzenes have been obtained from nitrobenzenes, the product composition being dependent on the reagents and conditions used In a recent communication [3], Alper and Paik described the selective conversion of nitrobenzenes into symmetrical azobenzenes in the presence of $Co_2(CO)_8$/benzene or (η^6-benzene)$Co_4(CO)_9$. We now report that the same conversion can be effected using $(MeCN)_3Cr(CO)_3$ in cyclohexane.

In connection with a kinetic study of S_NAr reactions of metal π-complexed halobenzenes [4], we prepared a series of tricarbonyl(η^6-halobenzene)chromium complexes by ligand-exchange reactions of $(MeCN)_3Cr(CO)_3$ with various halobenzenes in refluxing cyclohexane [5]. When a similar reaction was attempted using 4-nitrochlorobenzene (Ia),



(I) (II)

a; R = Cl d; R = Me
b; R = Br e; R = OMe
c; R = H

the corresponding benchrotrene was not obtained, an intractable mixture of insoluble chromium-containing materials resulting. However, chromatography of the organic extract on alumina afforded a low yield of 4,4'-dichloroazobenzene (IIa) which was identified by comparison with an authentic sample [6].

Similarly, we obtained a low yield of 4,4'-dibromoazobenzene (IIb) by reduction of 4-nitrobromobenzene (Ib) under the same reaction conditions. The presence of a halogen substituent in the benzene ring is not essential; similar treatment of nitrobenzene itself affords azobenzene (IIc) in comparable yield. However, the reaction is apparently inhibited by the presence of an electron-donating para-substituent in the nitrobenzene; no trace of the azobenzenes (IId,e) was found following treatment of the corresponding nitrobenzenes (Id,e). In these reactions, we did not detect the formation of products of less complete reduction of the nitro group. However, treatment of nitrosobenzene, a possible intermediate in the reduction of nitrobenzene, with $(MeCN)_3$-$Cr(CO)_3$ under the same reaction conditions likewise afforded azobenzene (IIc) although the product yield was not significantly improved.

The occurrence of nitro-group reduction in these reactions is associated with the presence of labile MeCN ligands attached to the metal atom in the organometallic reagent. No reduction product was detected when the nitrobenzene (Ia) was treated with $Cr(CO)_6$ in refluxing cyclohexane. Although we made no attempts to maximise product yields, it is clear that the nitrobenzene reductions reported herein proceed much less efficiently (5-7% conversion; ca. 10% yield based on unrecovered starting material) than those promoted by $Co_2(CO)_8$ in benzene (40-50% yield [3]).

Experimental

All reactions were carried out under an atmosphere of pure N_2. ^1H N.m.r. spectra were recorded for $CDCl_3$ solutions using a Perkin-Elmer R12A spectrometer at 60 MHz with Me_4Si as internal reference. Melting points are uncorrected. Petrol refers to the petroleum ether fraction b.p. 40-60^o. Chromatographies were carried out using neutral Spence Grade H alumina which had been deactivated by exposure to the atmosphere for 24 h.

Tris(acetonitrile)tricarbonylchromium

A solution of $Cr(CO)_6$ (2.2g; 0.01 mol) in oxygen-free acetonitrile (75ml) was refluxed with stirring for 16 h Evaporation of the solvent afforded a quantitative yield of $(MeCN)_3Cr(CO)_3$ [5] as an unstable yellow crystalline solid which was used immediately without further purification.

4,4'-Dichloroazobenzene (IIa)

A solution of 4-nitrochlorobenzene (1 57g; 0.01 mol) in oxygen-free cyclohexane (50ml) was added to $(MeCN)_3Cr(CO)_3$ [from 2.2g $Cr(CO)_6$] and the mixture was refluxed with stirring for 12 h The bulk of the solvent was then evaporated and the residual solution (decanted from insoluble chromium-containing compounds) was chromatographed. Petrol. ether (1.1) eluted the title compound (IIa) [80mg; 6.5% conversion; 8% yield based on starting material consumed], a yellow crystalline solid, m.p. 176-178^o (lit. [7] 188^o) and identical with an authentic sample [6]; ^1H n.m.r. τ2.0-2.8 (A_2B_2 multiplet). Further elution with the same solvent gave unchanged (Ia) (0.32g; 20% recovery)

4,4'-Dibromoazobenzene (IIb)

The previous experiment was repeated using 4-nitrobromobenzene (2.02g; 0.01 mol). Work-up as before followed by chromatography gave the title compound (IIb) (120mg; 7% conversion), a yellow crystalline solid, m.p. 200-202^o (lit. [8] 205^o), identical with an authentic sample [6]; ^1H n.m.r. τ1.8-2.8 (A_2B_2 multiplet).

Related reactions

Treatment of nitrobenzene or nitrosobenzene [9] with $(MeCN)_3Cr(CO)_3$ in refluxing cyclohexane and work-up as described earlier gave azobenzene (IIc) (5-7% conversion), m.p. 66-68°, which was identical with an authentic sample. Similar treatment of 4-nitrotoluene (Id) and 4-nitroanisole (Ie) with $(MeCN)_3Cr(CO)_3$, and of 4-nitrochlorobenzene (Ia) with $Cr(CO)_6$ in refluxing cyclohexane did not lead to the formation of the corresponding azobenzenes (IId, e, and a, respectively).

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