The Homogeneous Palladium-catalysed *ortho*-Chlorination of Azobenzene

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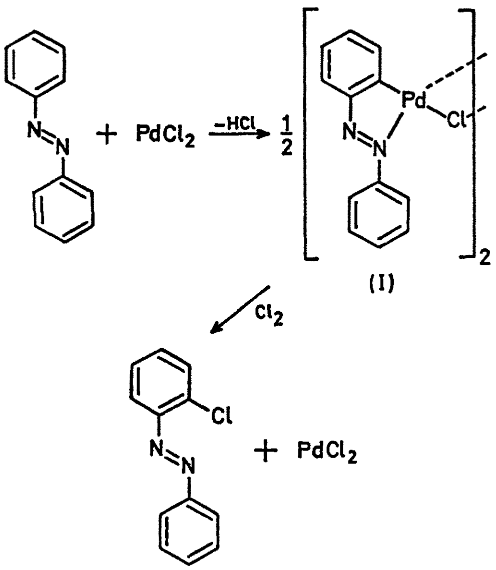
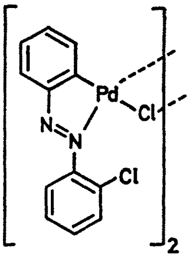
Summary The *ortho*-positions of azobenzene are chlorinated upon reaction with chlorine in the presence of catalytic quantities of $PdCl_2$.

WE report here the first example of a homogeneous coordination-catalysed chlorination reaction, that of azobenzene in the presence of $PdCl_2$. Azobenzene (5·5 mmole) and $PdCl_2$ (1·1 mmole) were stirred in 75 ml of a 2 : 1 mixture of dioxan and water at 85°. When the mixture became maroon, chlorine gas was slowly bubbled into the solution. The rate of Cl_2 addition was controlled to maintain the colour of the solution between yellow–orange and maroon. After 16 hr., the mixture became orange, and the reaction was stopped. The azobenzene products obtained from the reaction were isolated as an orange–red solid. This mixture was separated into its individual components by preparative g.l.c. to afford 2-chloroazobenzene (12%), 2,6-dichloroazobenzene (22%), 2,2′-dichloroazobenzene (30%), 2,6,2′-trichloroazobenzene (33%), and 2,6,2′,6′-tetrachloroazobenzene (3%). Spectral data are consistent with the assigned structures. Upon increasing the $PdCl_2$ concentration fivefold and with an extended reaction time, 2,6,2′,6′-tetrachloroazobenzene, m.p. 93—94°, was obtained as the major product in a 39% recrystallized yield.

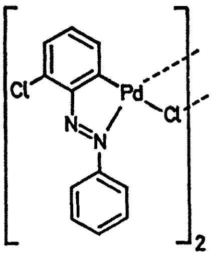


A productivity determination was conducted by treating 30 mmole of azobenzene and 1·0 mmole of $PdCl_2$ with chlorine. After 35 hr., the azobenzene product mixture was composed of azobenzene, 2-chloroazobenzene, 2,6-dichloroazobenzene, and 2,2′-dichloroazobenzene in a molar ratio of 11 : 29 : 1 : 1·4. This ratio corresponds to a turnover number of 24 for palladium.

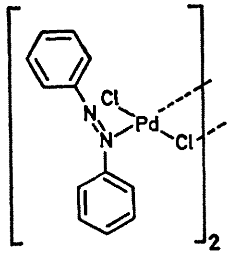
The reaction mechanism likely involves the addition of Cl_2 to a 2-(phenylazo)phenylpalladium complex. The maroon colour of the solution is characteristic of chloro-2-(phenylazo)phenylpalladium dimer (1).[1] Indeed, we have isolated this complex from the reaction mixture during early stages of the reaction. The cleavage of the carbon–metal σ-bond by Cl_2 would produce a carbon–chlorine bond and regenerate the $PdCl_2$ catalyst. At a later stage of the reaction, a red–brown solid, m.p. 281—283° (decomp.), was isolated which analysed for a 2-(2-chlorophenylazo)phenylpalladium complex (IIa), a 2-phenylazo-3-chlorophenylpalladium complex (IIb), or an azobenzene–$PdCl_2$ complex (III). Chlorination of this complex afforded a mixture of 2,2′-dichloroazobenzene and 2,6-dichloroazobenzene in a 4 : 1 ratio. The complex exhibits i.r. absorptions (CsI) at 232 (m), 262 (m,sh), and 282 (s) cm^{-1} which may be attributed to bridging Pd–Cl stretching vibrations. These data, along with the absence of a strong terminal Pd–Cl stretching vibration at *ca.* 355 cm^{-1},[2] suggest that the complex is a 4 : 1 mixture of (IIa) and (IIb).



(IIa)



(IIb)



(III)

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[1] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.
[2] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.