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PHOTOINDUCED REACTION OF AZOBENZENE WITH ACETYL CHLORIDE

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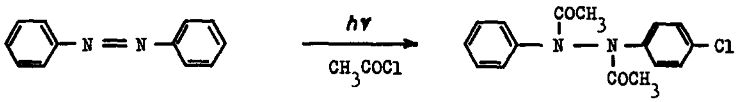
Some recent investigations of solvent effects in the previously reported[1-4] photochemical cyclization of azo compounds have led to the discovery of a photoinduced reaction between azobenzene (I) and acetyl chloride, from which N,N'-diacetyl-4-chlorohydrazobenzene (II) is obtained in excellent yield. The reaction occurs rapidly under the influence of sunlight or light from a high pressure mercury lamp. No evidence of a dark reaction could be found, even when solutions of azobenzene in acetyl chloride were refluxed for long periods.



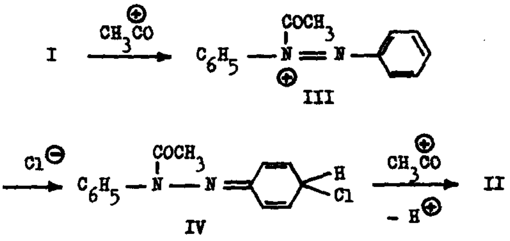
I II

In one of several experiments, a solution of azobenzene (100 mg) in acetyl chloride (50 ml) was irradiated for 1.5 hr with a Philips HP 125 W mercury-quartz lamp in a water-cooled Pyrex photochemical reactor.[3] After evaporation of the solvent, the residue was redissolved in chloroform and chromatographed on a column of silica. Only one compound (140 mg), b.p. 132-136° / 0.02 mm, could be isolated from the eluate and this was shown to be N,N'-diacetyl-4-chlorohydrazobenzene (84% yield). Analytical data indicated the formula $C_{16}H_{15}ClN_2O_2$, and the molecular structure was deduced from infrared and n.m.r. spectral data (see below) in conjunction with the fact that the compound was converted to 4-chloroazobenzene (92% yield) by hydrolysis in aqueous ethanolic sodium hydroxide, followed by oxidation of the de-acetylated hydrazo compound with sodium hypobromite. The identity of the hydrolysis-oxidation product was confirmed by direct comparison (mixed m.p. and infrared spectrum) with an authentic sample of 4-chloroazobenzene available from earlier work.[4]

The infrared spectrum (CCl_4) of *N*,*N'*-diacetyl-4-chlorohydrazobenzene showed *inter alia* bands at 1710 and 1690 cm^{-1} (C=O). The n.m.r. spectrum ($CDCl_3$), which was determined with tetramethylsilane as an internal standard, showed a sharp singlet at τ 8.03 (6 protons), assigned to the acetyl groups, and a somewhat broader singlet at τ 2.69 (9 protons), assigned to the aromatic ring-protons.

As further confirmatory evidence for the constitution of the photoproduct, *N*,*N'*-diacetyl-4-chlorohydrazobenzene was separately prepared by reduction of authentic 4-chloroazobenzene with lithium aluminium hydride, followed by exhaustive acetylation of the hydrazo compound with acetyl chloride. The infrared spectrum of this product was identical with that of the photoproduct, and neither of the spectral curves displayed absorption attributable to N-H stretching.

In view of the selective *p*-substitution by chlorine it seems probable that the photochemical formation of *N*,*N'*-diacetyl-4-chlorohydrazobenzene is an ionic process. Recent reports[5-9] of several photoinduced nucleophilic substitution reactions of aromatic compounds are of particular interest in this connection, and the following mechanistic pathway, (I→III→IV→II), involving acetylium and chloride ions, is tentatively suggested to account for the present reaction.



Further experiments towards elucidation of the mechanism are in hand, and the scope of the reaction, with respect to azo compounds and acid halides generally, is also being investigated.

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