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PHOTOCHEMICAL CYCLODEHYDROGENATION OF CONJUGATE ACIDS OF AZOBENZENE WITH LEWIS ACIDS

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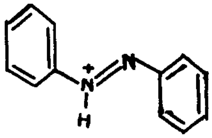
Irradiation of azobenzene in strongly acidic solutions leads to the formation of benzo[c]cinnoline (III) by cyclodehydrogenation[1]. Subsequent work[2] has shown that cyclization is preceded by rapid trans $\rightleftharpoons$ cis isomerization of the cations (I $\rightleftharpoons$ II). Hugelshofer[3] et al have reported the formation of benzo[c]-cinnoline when an acetic acid solution of azobenzene was irradiated in presence of $FeCl_3$. Attempts have been made to effect the photochemical cyclodehydrogenation of azobenzene in nonacidic media, but these have been unsuccessful.[4]



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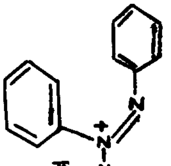

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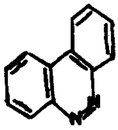

III

Here we report the photocyclization of the conjugate acid of azobenzene with $AlCl_3$ in nonpolar solvents. The recent report of the complex formation of azobenzene and its derivatives with acceptor halides in nonpolar solvents[5], prompted us to study the photochemical behaviour of these. Since the lowest transition of these azobenzene complexes would be of the $\pi-\pi^*$ type, which is necessary for cyclization[6], it was expected that cyclization ~~will~~ would occur.

A water-cooled Pyrex photochemical reactor with a Philips 125W high pressure mercury-quartz lamp was used for these experiments. A solution of $AlCl_3$ (1.5 g) in dry 1,2-dichloroethane (110 ml.) was refluxed for three hours to render it almost free from any preformed HCl. After addition of azobenzene (500 mg), the solution was irradiated till the reaction appeared to be complete

(50 hrs.). Working up and chromatography on alumina yielded unchanged azobenzene (45 mg), benzo[c]cinnoline (260 mg), benzidine (110 mg) and some unidentified resinuous product.

The above results clearly show that this photochemical reaction proceeds mainly by a disproportionation process. By analogy with the detailed mechanism proposed for the reaction in sulphuric acid,[7] it would appear that the role of $AlCl_3$ in this case is that of a Lewis acid and that dehydrogenation of a probable ring-closed dihydro intermediate complexed with $AlCl_3$ is effected by the conjugate acid of azobenzene. Thus for every molecule of azobenzene that undergoes cyclodehydrogenation, one molecule is reduced to hydrazobenzene, which rearranges to benzidine under the acidic condition arising when the reaction mixture is worked up. The slightly higher yield of benzo[c]cinnoline and hence the lower yield of benzidine may be explained as due to the formation of azobenzene by the possible disproportionation of the hydrazobenzene.

Other solvents which were found to be satisfactory were $CHCl_3$, CH_2Cl_2 and CCl_4. The usefulness of other acceptor halides such as $ZrCl_4$, $TiCl_4$, $SbCl_5$, and $SnCl_4$ in the photocyclizations of azobenzenes is under study.

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