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PHOTOCHEMICAL CYCLODEHYDROGENATION OF LEWIS ACID-CONJUGATES OF AZOBENZENES[a]

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Abstract—Irradiation of the conjugate acids of azobenzene (**1a**) with Lewis acids like anhydrous $AlCl_3$, anhydrous $SnCl_4$ and anhydrous $FeCl_3$ in 1,2-dichloroethane results in cyclodehydrogenation to benzo[*c*]cinnoline (**2a**). The formation of benzidine (**3a**) along with **2a** suggests that the reaction is a photochemical disproportionation. The absorption spectra of the conjugate acids in 1,2-dichloroethane reveal that inversion of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ singlet state energies occurs on complexation of the azo nitrogen with the Lewis acid. Irradiation of the Lewis acid-conjugates of 2-methylazobenzene (**1b**), 2,2′-dimethylazobenzene (**1c**), 4,4′-dimethylazobenzene (**1d**) and 4-chloroazobenzene (**1e**) also results in cyclodehydrogenation.

Azobenzenes do not undergo photochemical cyclodehydrogenation under the neutral conditions[1] in which stilbenes,[2] diphenylamines[3] and Schiff-bases[4] undergo photocyclodehydrogenation. The failure of azobenzene to photocyclize in neutral solutions was attributed[5] to the fact that the lowest excited state under these conditions is of the $n \rightarrow \pi^*$ type. Jaffe[5] examined the spectrum of azobenzene in organic solvents and assigned the longest wavelength band at 420 nm to the $n \rightarrow \pi^*$ transition. On the other hand, the absorption band in the longest wavelength region of acidic solutions of azobenzene has been assigned to the $\pi \rightarrow \pi^*$ transition.[6] Irradiation of azobenzene in acidic solution has been shown to undergo cyclodehydrogenation by a photochemical disproportionation mechanism.[7,8] Quantum yield data[9] for the photochemical cyclization of azobenzene in sulphuric acid of different normalities have shown clearly that the conjugate acid of azobenzene, and not the free base, is the species which undergoes ring-closure.

This phenomenon and the possibility of complex formation of azobenzene and its derivatives with acceptor halides in 1,2-dichloroethane[10] prompted an examination of the photochemical behaviours of these complexes. Since the lowest transition of these azobenzene-complexes would be of the $\pi \rightarrow \pi^*$ type it was expected that cyclization would occur.

Irradiation of azobenzene (**1a**) in 1,2-dichloroethane in presence of anhydrous $AlCl_3$, followed by working-up and chromatography on a column of alumina yielded benzo[*c*]cinnoline (**2a**; 57%) and benzidine (**3a**; 25%). To exclude any hydrochloric acid, formed by the hydrolysis of anhydrous $AlCl_3$ by moisture, before the addition of azobenzene, the solvent was refluxed with anhydrous $AlCl_3$ for three hours. Similar irradiations of azobenzene with anhydrous $SnCl_4$ and anhydrous $FeCl_3$ also gave the same products in comparable yields.

The above results clearly show that this photochemical reaction proceeds by a disproportionation mechanism[8] as in the cases of the photochemical reactions of azobenzenes in 22N sulphuric acid. Thus, for every molecule of the azobenzene-conjugate acid that cyclizes, another molecule of the azobenzene-conjugate acid acts as a hydrogen abstractor, itself getting reduced to the hydrazobenzene (**4**). This hydrazobenzene rearranges to benzidine under the acidic conditions arising when the reaction mixture is worked-up. This suggestion demands the formation of benzo[*c*]cinnoline and benzidine in equimolecular quantities. Then, the higher yield of benzo[*c*]cinnoline, and hence the lower yield of benzidine may be explained as due to the possible disproportionation of hydrazobenzene[11,12] to azobenzene and aniline. This azobenzene undergoes cyclization to give more benzo[*c*]cinnoline. Thus, ultimately 66·66% of benzo[*c*]cinnoline could be expected, if all the hydrazobenzene formed undergoes disproportionation.

Irradiation of 2-methylazobenzene (**1b**), 2,2′-dimethylazobenzene (**1c**), 4,4′-dimethylazobenzene (**1d**) and 4-chloroazobenzene (**1e**) under similar conditions as that of azobenzene resulted in cyclodehydrogenation and benzo[*c*]cinnolines were isolated in comparable yields. In the case of 2-methyl- and 2,2′-dimethylazobenzenes in addition to the expected benzo[*c*]cinnolines, those formed by the ejection of a methyl group

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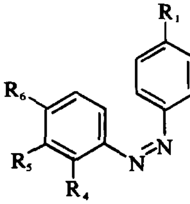
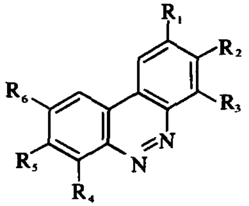
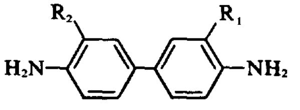


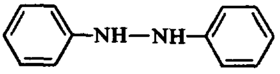
1a: $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$
1b: $R_3 = Me$; $R_1 = R_2 = R_4 = R_5 = R_6 = H$
1c: $R_3 = R_4 = Me$; $R_1 = R_2 = R_5 = R_6 = H$
1d: $R_1 = R_6 = Me$; $R_2 = R_3 = R_4 = R_5 = H$
1e: $R_1 = Cl$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$



2a: $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$
2b: $R_3 = Me$; $R_1 = R_2 = R_4 = R_5 = R_6 = H$
2c: $R_3 = R_4 = Me$; $R_1 = R_2 = R_5 = R_6 = H$
2d: $R_1 = R_6 = Me$; $R_2 = R_3 = R_4 = R_5 = H$
2e: $R_1 = Cl$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$



3a: $R_1 = R_2 = H$
3b: $R_1 = R_2 = Me$



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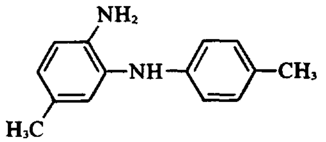

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from the point of cyclization were also isolated in small quantities. The duration of irradiation, various products observed with the three Lewis acids used and their yields are given in Table 1.

Hugelshofer *et al.*[2] and later Lewis and Mayfield[13] examined the photochemical behaviour of azobenzene in acetic acid containing excess $FeCl_3$ or excess $AlCl_3$. In these cases cyclodehydrogenation occured to some extent. To obtain a clear insight into the mechanism of the reaction of azobenzene in presence of Lewis acids in 1,2-dichloroethane, a comparative study of the absorption spectra of

Table 1

	In presence of anhyd $AlCl_3$		In presence of anhyd $SnCl_4$		In presence of anhyd $FeCl_3$	
Azo compound irradiated	Irradn time (hrs)	Products (yield[a])	Irradn time	Products (yield[a])	Irradn time (hrs)	Products (yield[a])
Azobenzene (**1a**)	50	Benzo[*c*]cinnoline (**2a**, 57%); benzidine (**3a**, 25%)	50	**2a** (60%); **3a** (8%)	50	**2a** (45%); **3a** (11%)
2-Methylazobenzene (**1b**)	70	4-Methylbenzo[*c*]cinnoline (**2b**, 51%); **2a** (11%)	50	**2b** (58%); **2a** (9%)	60	**2b** (50%); **2a** (5%)
2,2′-Dimethylazobenzene (**1c**)	80	4,7-Dimethylbenzo[*c*]cinnoline (**2c**, 40%); **2b** (10%); 3,3′-dimethyl benzidine (**3b**, 20%)	80	**2c** (47%); **2b** (10%); **3b** (9%)	80	**2c** (43%); **2b** (9%) **3b** (14%)
4,4′-Dimethylazobenzene (**1d**)	90	2,9-Dimethylbenzo[*c*]cinnoline (**2d**, 56%); 2-amino-4′,5-dimethyldiphenyl amine (**5**, 11%)	90	**2d** (57%); **5** (6%)	90	**2d** (51%); **5** (9%)
4-Chloroazobenzene (**1e**)	60	2-Chlorobenzo[*c*]cinnoline (**2e**, 40%)	60	**2e** (49%)	60	**2e** (45%)

[a] W.r.t. the azo compound undergone change.

azobenzene in (a) 1,2-dichloroethane, (b) in concentrated sulphuric acid, (c) in 1,2-dichloroethane in presence of anhydrous $AlCl_3$, (d) in acetic acid and (e) in acetic acid in presence of anhydrous $AlCl_3$, was made.

The absorption band at 315 nm (log ε, 4·36) in 1,2-dichloroethane due to the high energy $\pi \rightarrow \pi^*$ excitation was shifted to 435 nm (log ε, 4·1) in sulphuric acid solutions (Fig 1) and to 430 nm (log ε, 4·2) in 1,2-dichloroethane in presence of anhydrous $AlCl_3$ (Fig 2). But the $\pi \rightarrow \pi^*$ band did not show a marked shift in acetic acid containing $AlCl_3$ (Fig 2). These reveal that complexation of the azo nitrogen is almost complete in 1,2-dichloroethane in presence of anhydrous $AlCl_3$, whereas it is insignificant in acetic acid containing anhydrous $AlCl_3$. Thus the $\pi \rightarrow \pi^*$ excitation becomes the lowest photoexcited state for the azobenzene-complexes in 1,2-dichloroethane.

From the above observations, it is evident that one or more steps of the photoreaction in 1,2-dichloroethane are dependent on the azobenzene being complexed with the Lewis acid. Thus, by analogy with the mechanism proposed by Badger *et al* for the photoreaction in sulphuric acid the mechanism may be suggested as follows: (Scheme 1); the cyclizing species is probably the first excited singlet state in which the positive charge originally represented on the azo nitrogen in the ground state of the *cis*-conjugate acid (A) is more effectively shared with the carbon atoms at 2′, 4′ and 6′ positions. This implies that the conjugate acid should have a higher p*K* value in the excited state. This is consistent with the observation that the energy of the $\pi \rightarrow \pi^*$ transition in free azobenzene (to which 315 nm band is assigned) is lowered on complexation with the Lewis acid. These conclusions are in agreement with the observations of Steininger and Gutmann who investigated the dissociation constants of the complexes of azobenzene with acceptor halides in 1,2-dichloroethane.[10]

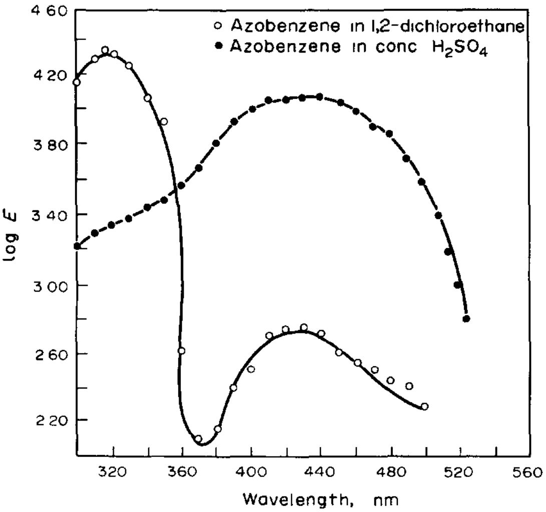


Fig 1.

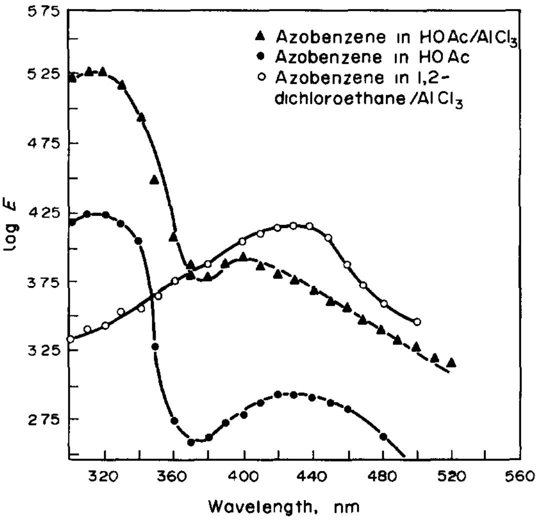
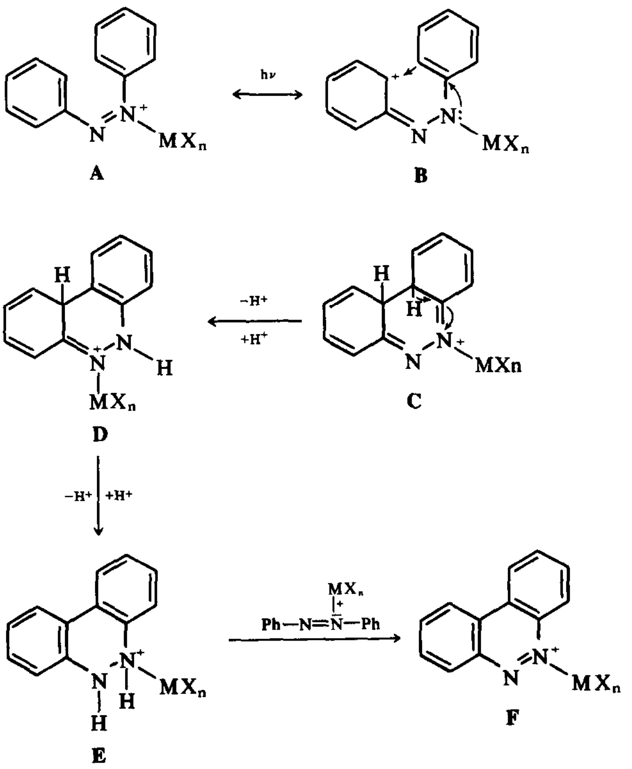


Fig 2.

Structure B may therefore be considered as an important excited state resonance structure, and this is mechanistically significant, if the ring-closure step of the reaction involves an excited state of the $\pi \rightarrow \pi^*$ type. B then cyclizes to give the conjugate acid of 10*a*,10*b*-dihydrobenzo[*c*]cinnoline (**C**), which in turn would undergo two fast prototropic rearrangements in succession giving the conjugate acid of 5,6 - dihydrobenzo[*c*]cinnoline (**E**) by way of the complexed 5,10*a* - dihydrobenzo[*c*]cinnoline (**D**). This is oxidised to the fully aromatic compound (**F**) on interaction with the conjugate acid of azobenzene. Thus, the mechanism of the cyclodehydrogenation of these azobenzene-Lewis acid conjugates is essentially the same as that suggested by Badger *et al*[9] for the reaction in concentrated sulphuric acid. The photochemical cyclodehydrogenation observed in acetic acid containing Lewis acids[2,13] probably results from the formation of azobenzene-conjugate acid with the hydrochloric acid formed.

EXPERIMENTAL

Preparation of azobenzenes. Azobenzene, m.p. 68°, was obtained by chromatography of technical azobenzene (Fluka) on alumina, followed by recrystallisation from EtOH. 2-Methylazobenzene, b.p., 179°/15 mm[14] and 4-chloroazobenzene, m.p., 87°[15] were prepared by the condensation of nitrosobenzene with *o*-toluidine and *p*-chloroaniline respectively in glacial AcOH followed by working-up and chromatography. 2,2′-dimethylazobenzene, m.p. 55°[16] and 4,4′-dimethyl azobenzene m.p. 145°[16] were prepared by the reduction of *o*-nitrotoluene and *p*-nitrotoluene respectively with zinc



Scheme 1

dust and NaOH in MeOH followed by working-up and chromatography on alumina.

Photochemical reactors. Irradiations were carried out with a Phillips HPK 125 W mercury-quartz lamp in a water-cooled pyrex apparatus of 160 ml capacity or in a Hanovia one litre photochemical reactor. In both the cases the lamp was surrounded by a cylindrical water-jacket which was in turn surrounded by a jacket containing the soln to be irradiated.

Irradiation of azobenzene (**1a**). A soln of anhyd AlCl$_3$ (1·5 g) in dry 1,2-dichloroethane (110 ml) was refluxed for 3 h to render it free from any HCl. After addition of azobenzene (0·5 g), the soln was irradiated at ambient temp for 50 h. Water (50 ml) was added to the mixture and the 1,2-dichloroethane was removed by distillation. The aqueous soln was neutrallised with NaHCO$_3$ (5 g) and then extracted with chloroform (60 ml). Evaporated the solvent and the residue (0·43 g) was chromatographed on an alumina column. Elution with light petroleum (60–80°) gave the unchanged azobenzene (45 mg). Further elution with benzene-CHCl$_3$ mixture (1:7, v/v) resulted in the separation of an yellow fluorescent band. Evaporation of the eluate (140 ml) and recrystallisation of the residue from aqueous EtOH gave **2a** as yellow needles (260 mg), m.p. 156°, not depressed by admixture with an authentic specimen.[8] Further elution with CHCl$_3$ and evaporation of the CHCl$_3$ eluate (50 ml) followed by recrystallisation of the residue from aqueous EtOH afforded **3a** (110 mg) as colourless plates, m.p. 126°, alone or when admixed with an authentic specimen. Final elution with alcohol gave a resinuous material (25 mg) which could not be crystallised.

Similar irradiation and working-up in presence of anhyd SnCl$_4$ and anhyd FeCl$_3$ gave the same products in comparable yields (see Table).

Irradiation of 2-*methylazobenzene* (**1b**). **1b** (200 mg) in 1,2-dichloroethane (850 ml) in presence of anhyd AlCl$_3$ (1 g) was irradiated in the Hanovia one litre photochemical reactor for 70 h. The mixture was added to water (50 ml) and the organic solvent was distilled off. The aqueous soln was neutrallised with NaHCO$_3$ (5 g) and was then extracted with ether. The ether extract was washed, dried and evaporated. The residue was chromatographed on alumina. Elution with light petroleum gave unchanged **1b** (15 mg). Then the column was eluted with benzene. Evaporation of this fraction followed by crystallisation of the residue from EtOH gave **2b** (95 mg) as yellow needles, m.p. 129°, alone or when admixed with an authentic sample.[8] Elution with benzene-CHCl$_3$ mixture (9:1, v/v) gave benzo[*c*]cinnoline (20 mg) m.p. and m.m.p. 156°. Final elution with CHCl$_3$ gave a brown oily material (35 mg) which could not be characterised.

Similar irradiation of **1b** with the other two Lewis acids also gave the cyclodehydrogenated products in comparable yields (see Table).

Irradiation of 2,2′-*dimethylazobenzene* (**1c**). **1c** (200 mg) in 1,2-dichloroethane (850 ml) in presence of anhyd AlCl$_3$ (1 g) was irradiated for 80 h in the reactor. Working-up of the mixture as above followed by chromatography of the benzene extract on an alumina column gave as the first fraction **2c** (90 mg) as yellow needles from aqueous EtOH, with m.p. 170° (lit[8] 170°), alone or admixed with an authentic sample. Further elution gave **2b** (20 mg), m.p. and m.m.p. 129° and an unidentified product (10 mg), m.p.

142°, showing absorptions at 252 nm and at 380 nm characteristic of a benzo[*c*]cinnoline.[8] Final elution with ether gave a solid (40 mg) which on recrystallisation from aqueous EtOH gave light brown needles of **3b**, m.p. 126° (lit[17] 129°).

Irradiation of **1c** in presence of the other two Lewis acids also gave the same products in almost identical yields (Table).

Irradiation of 4,4′-*dimethylazobenzene* (**1d**). Irradiation of **1d** (200 mg) for 90 h under the conditions as above, followed by working-up and chromatography of the benzene extract gave unchanged **1d** (15 mg) as the first fraction. Evaporation of the following fraction followed by recrystallisation of the residue from aqueous EtOH afforded **5**, (20 mg) as colourless flakes, m.p. 108° (lit[18] 107°). Further elution of the chromatorgram with benzene-$CHCl_3$ mixture gave, **2d**, (105 mg) as pale yellow needles (from EtOH) with m.p. 190°, alone or on admixture with an authentic sample.[8]

Irradiations in presence of the other two Lewis acids under identical conditions and similar working-up procedures gave the same products in comparable yields (Table).

Irradiation of 4-*chloroazobenzene* (**1e**). Irradiation of **1e** (200 mg) under the conditions as above followed by working-up and chromatography of the benzene extract on an alumina column, gave unchanged **1e** (40 mg) as the first fraction. Further elution of the chromatogram with benzene-$CHCl_3$ mixture (9:1, v/v) gave an yellow solid which on recrystallisation from, EtOH afforded yellow needles of **2c** (65 mg), m.p. 215° alone or on admixture with an authentic sample.[19] Final elution with $CHCl_3$ and evaporation of this eluate gave a dark oily material which could not be crystallised.

Compound **2e** was also obtained in comparable yields from the irradiations of **1e** in the presence of the other two Lewis acids (Table).

Absorption spectra. A Beckmann DU-2-spectrophotometer was used for the determination of the absorption spectra. 10^{-4} M soln of azobenzene in 1,2-dichloroethane, azobenzene in conc H_2SO_4, azobenzene in HOAc, azobenzene-$AlCl_3$ complex in 1,2-dichloroethane, and azobenzene-$AlCl_3$ complex in HOAc were used for the measurements. The logarithms of the extinction coefficients were plotted against absorbing wavelengths (Figs 1 and 2).

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