Preparation and Photolysis of Diphenyldiazasuccinic Anhydride

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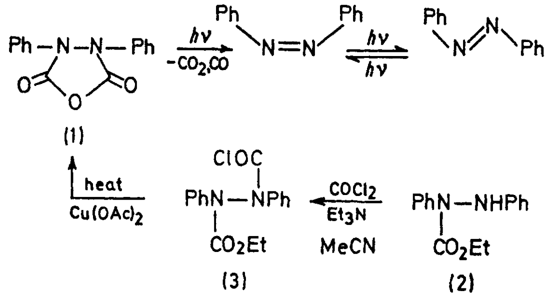
Summary The hitherto inaccessible diphenyldiazasuccinic anhydride has been prepared and found to photodecompose to *cis*-azobenzene together with carbon monoxide and carbon dioxide *via* a new type of photoelimination reaction.

The finding that monoazasuccinic anhydrides give on irradiation imines, carbon dioxide, and carbon monoxide[1] led us to examine the synthesis and photolysis of the hitherto unknown diphenyldiazasuccinic anhydride (diphenylcarbamic anhydride) (**1**).



As has been reported,[2] no reaction could be observed between ethyl diphenylhydrazinecarboxylate (**2**) and phosgene in toluene at room temperature. In toluene under reflux we found that reaction occurred to give benzidine rearrangement products, as shown by the presence of *p*-substituted phenyl and NH peaks in the i.r. spectrum of the recovered material. Subsequent investigation showed that the acid chloride (**3**) could only be formed in a polar solvent such as acetonitrile at 0° in the presence of an excess of triethylamine to prevent rearrangement. Removal of the solvent followed by extraction with boiling hexane gave, on cooling, the acid chloride (**3**) as an oil. The *p*-bromoanilide derivative, m.p. 137—138°, *m/e* 435 analysed satisfactorily.

(**3**) is stable to 150° and yields tars but no anhydride (**1**) on heating to higher temperatures. However, heating 15 g of (**3**) in the presence of 1 g of copper(II) acetate to 145° for 70 min gives 35% of the required anhydride (**1**), m.p. 111–112° (hexane). The compound analyses correctly, and shows *m/e* 254 and major peaks for loss of CO_2, followed by CO, in the mass spectrum. It shows peaks in the i.r. (Nujol) at 1840 and 1780 cm^{-1} (C=O) and u.v. (hexane) at 234 (log ϵ 4·20), 266sh (3·08) and 274sh nm (2·83).

The anhydride (**1**) when treated with fuming nitric acid in acetic acid and acetic anhydride at room temperature affords 4-nitrodiphenyldiazasuccinic anhydride, m.p. 136—138° (60%). This compound is photostable.

On irradiation with 254 nm light in hexane or ethanol, (**1**) yields yellow-orange solutions from which *cis*- and *trans*-azobenzene can be isolated by chromatography.† Multicomponent spectroscopic analysis shows the initial product in hexane is 90% *cis*-azobenzene, formed with a quantum yield of 0·15. However, photoequilibration of azobenzene by 254 nm light is rapid ($\phi_{c\rightarrow t}$ = 0·44; $\phi_{t\rightarrow c}$ = 0·13),[3] and further irradiation leads to a mixture which is 11% *cis*, a value very close to the reported photostationary value of 8%.[3] The maximum observed conversion into azobenzene was 82%.

Since the photodecomposition of (**1**), $E_T \leqslant$ 61 kcal,‡ was neither sensitized by 0·2N-benzophenone, E_T = 70 kcal, nor quenched by 0·1N-piperylene, E_T = 59 kcal, it is probable that reaction occurs *via* the singlet state. The observed high initial yield of *cis*-azobenzene also suggests reaction *via* the singlet, as triplet azobenzene, if formed, would undergo isomerization.

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† The same products are formed thermally on heating (**1**) at 210°.

‡ At 77 K in ethanol, the longest wavelength phosphorescence band maximum of (**1**) is at 470 nm.

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[2] C. D. Hurd and F. F. Cesark, *J. Amer. Chem. Soc.*, 1967, **89**, 1417.
[3] G. Zimmerman, L. Chow, and U. Paik, *J. Amer. Chem. Soc.*, 1958, **80**, 3528.