

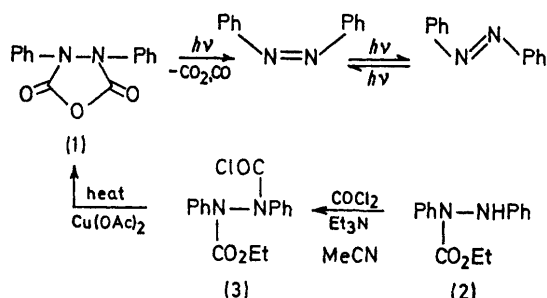
Preparation and Photolysis of Diphenyldiazasuccinic Anhydride

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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 monoxide¹ 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 ($\log \epsilon$ 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.† Multi-component 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 ($\phi_{e \rightarrow t} = 0.44$; $\phi_{t \rightarrow e} = 0.13$),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), $E_T \leq 61$ 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.

¹ W. A. Henderson, jun., and A. Zweig, *Tetrahedron*, 1971, **27**, 5307.² 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.