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PHOTOCHEMICAL DECARBOXYLATION OF AZOBENZENE-2-CARBOXYLIC ACIDS

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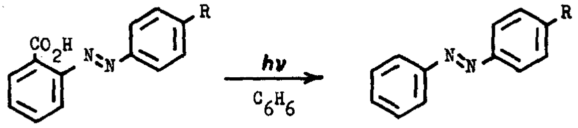
According to a recent communication (1) acetylsalicylic acid is de-acetoxylated to benzoic acid when irradiated in acetic acid solution with a medium-pressure mercury arc. The presence of the ortho-carboxy substituent appears to be necessary for de-acetoxylation, as m- and p-acetoxybenzoic acids and ethyl o-acetoxybenzoate under the same conditions yield m- and p-hydroxybenzoic acids and ethyl salicylate, respectively.

We now report an example of photochemical decarboxylation which is clearly of related interest to the foregoing reaction.

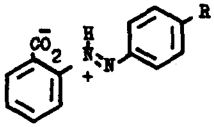


I II

When azobenzene-2-carboxylic acid (I; R = H) and its 4'-methyl, 4'-chloro, and 4'-dimethylamino derivatives (I; R = Me, Cl, and NMe_2) are irradiated in benzene with a high-pressure mercury lamp, the corresponding decarboxylated azo compounds (II) are formed. It is significant that neither azobenzene-3-carboxylic acid nor azobenzene-4-carboxylic acid undergoes photochemical decarboxylation under these conditions, even when irradiation is extended for much longer periods.

A water-cooled Pyrex photochemical reactor (2), fitted with a Philips HP 125W mercury-quartz lamp, was used for these experiments. Each azobenzene-2-carboxylic acid (200 mg) was irradiated in a solution in benzene (110 ml) for 50 hr. After irradiation, the solution was concentrated to a small volume (10 ml) and subjected to chromatography, alumina being used as the adsorbent in the case of the 4'-dimethylamino compound, and silica gel in the remaining cases. Each decarboxylated azo compound (10-12 mg) was eluted well in advance of the unchanged carboxylic acid. The four decarboxylated products were identified by direct comparison (mixed m.p. and infrared spectra) with authentic samples available from earlier work (2-4).

The carboxy group in 4'-dimethylaminoazobenzene-2-carboxylic acid has been shown to be intramolecularly hydrogen-bonded to the adjacent azo-nitrogen atom (5,6), and we have confirmed from infrared spectra in carbon tetrachloride solutions that azobenzene-2-carboxylic acid and its 4'-methyl and 4'-chloro derivatives are likewise intramolecularly hydrogen-bonded. These observations, and the lack of photochemical reactivity of azobenzene-3- and azobenzene-4-carboxylic acids, indicate that zwitterionic forms (III) of the 2-carboxylic acids could play an essential role in photochemical decarboxylation.



III

When azobenzenes, containing a methyl, chloro, iodo, or carboxy substituent in the 2-position, are photochemically cyclodehydrogenated in 22 N sulphuric acid small quantities of unsubstituted benzo[c]cinnoline are formed, although the main products are the corresponding 4-substituted benzo[*c*]cinnolines (2,3). Available evidence (2,3,7) suggests that ejection of substituents in these reactions is caused by ring-closure at the 2-position. It is relevant that no benzo[*c*]cinnoline derivatives were formed on irradiation of the azobenzene-2-carboxylic acids in benzene.

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