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Photochemistry of N-Phenylbenzenecarbohydroxamic Acid [1]

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N-Phenylbenzenecarbohydroxamic acid undergoes a photoreaction in cyclohexane and methanol to give benzanilide as a major product.

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Photochemie von N-Phenylbenzolcarbohydroxamsäure

N-Phenylbenzolcarbohydroxamsäure ergibt in einer Photoreaktion (in Cyclohexan und Methanol) Benzanilid als Hauptprodukt.

Introduction

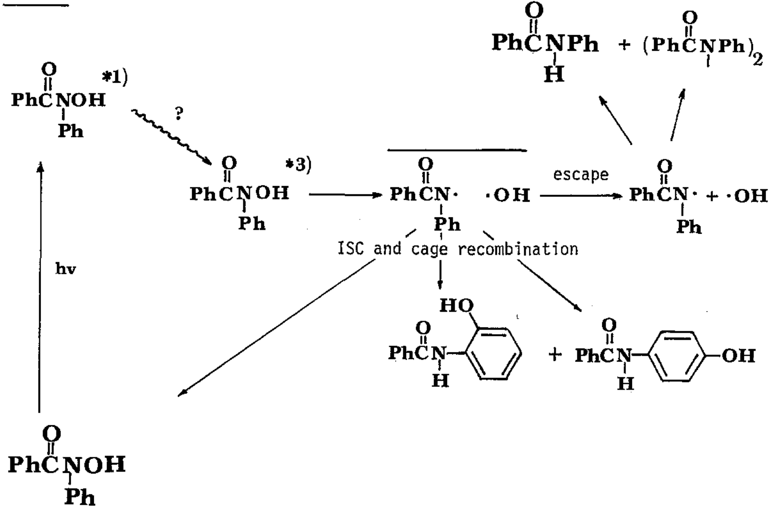
Whereas hydroxamic acids and metal hydroxamates are known to be photostable [2], recent discovery of oscillation phenomena in the fluorescence intensity of some aromatic hydroxamic acids [3] suggests that they can undergo photochemical reactions. N-Phenylbenzenecarbohydroxamic acid (**1**) has the structural units of benzanilide and phenylhydroxylamine and therefore is expected to be most photolabile. The former chromophore is established to undergo the photo-*Fries* rearrangement [4]. The latter gives rise to a nitroxide radical due to one-electron oxidation [5]. Deoxygenation is considered to be another possibility.

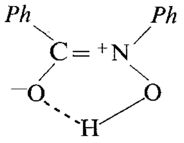
Results and Discussion

Irradiation of **1** in a quartz apparatus was carried out in ambient (cyclohexane and methanol) and basic (aqueous methanol, 1 : 1, $pH > 12$)

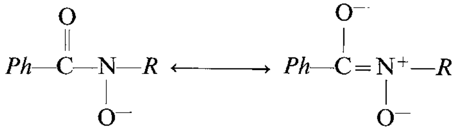
media. The progress of the reactions was followed by HPLC under the conditions standardized previously [6]. In a typical run in cyclohexane, the following products were obtained: benzanilide (**2**) (65%), 1,2-dibenzoyl-1,2-diphenylhydrazine (**3**) (15%), N-benzoyl-*o*-hydroxyaniline (10%) and N-benzoyl-*p*-hydroxyaniline (3%). In methanol and its basic medium, the yields of **1** were 70 and 50%, respectively. The quantum yields for the disappearance of **1** were 0.067, 0.007 and 0.012 in cyclohexane, methanol and basic methanol, respectively. The formation of **1** is accounted for by the initial homolysis of the N—O bond (Scheme 1). In an ESR cavity, signals due to an acylnitroxide were detected [7]. It is not clear if this is an intermediate or a side product. The failure of the amide rearrangement is ascribed to the high C = N double bond character due to the contribution of hydrogen bond [2]:

Scheme 1





A ca. 30 nm bathochromic shift of the absorption maximum of **1** is observed on formation of the anion **1a** (Fig. 1). Our ^{17}O NMR study has shown that the anion of N-substituted derivatives has resonance structures [2]:



$$Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O^-}{|}}{N}{-}R \longleftrightarrow Ph{-}\overset{\overset{\displaystyle O^-}{|}}{C}{=}\underset{\underset{\displaystyle O^-}{|}}{N^+}{-}R$$

1a **1a′**

Structure **1a′** resembles the nitrone chromophore which is known to undergo photoreactions via oxaziridine intermediates [8]. A similar mechanism could be suggested for the photoreaction of **1** in basic media.

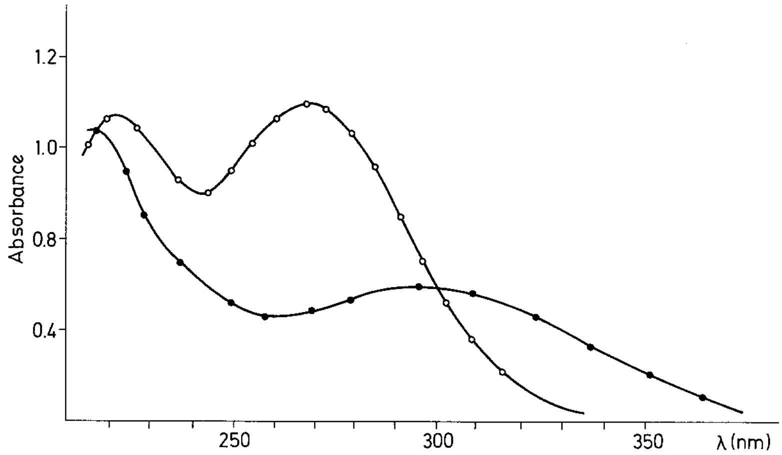


Fig. 1. UV spectra of N-phenylbenzenehydroxamic acid ($c = 7 \cdot 10^{-5} M$): ○—○—○ methanol; ●—●—● methanol/NaOH(aq) = 1 : 1, $pH \sim 13$

Experimental

N-Phenylbenzenecarbohydroxamic acid (**1**) was prepared and purified according to the Ref. [9]. Its melting points and analytical data agreed nicely with those reported in Ref. [10]. The authentic samples of **2**, **3**, and N-benzoyl-*o*- and *p*-hydroxyanilines were commercially available. Solvents were from E. Merck.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Elemental analyses were performed with a Perkin-Elmer 240 B analyzer. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer 377 spectrometer. ^{1}H NMR spectra were run on a Varian A-60 spectrometer with *TMS* as an internal standard. UV-VIS spectra were measured on a PU-8800 (Pye Unicam) spectrophotometer. Preparative irradiations were performed with a low pressure mercury lamp (Hanan St-40 W). HBO-50 mercury lamp (Carl Zeiss, Jena) was used for determination of the reaction quantum yields. HPLC was carried out on a HPLC LKB chromatograph equipped with a LKB 2150 HPLC pump, a LKB 2140 rapid detector, a LKB 2155 HPLC column oven, and an Olivetti personal computer M-24.

Preparative irradiations of **1** ($c = 2 \cdot 10^{-2}\,M$) were carried out in a quartz cell under nitrogen atmosphere at 0 °C. After ca. one hour irradiation, the solvent was removed under reduced pressure and the residue was separated by a Lobar column using $CHCl_3$/hexane (1 : 1) as an eluent. The products were characterized by comparison of their m.p., ^1H NMR, IR and MS data with those of the authentic samples.

For quantum yield determination, the stirred solutions of **1** ($c = 1 \cdot 10^{-4}\,M$) were irradiated in a quartz cell through a KI/I_2 solution filter at room temperature. The conversion was kept at 30% or less. The potassium ferrioxalate actinometry was used. The consumption of **1** was followed by HPLC [6].

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