

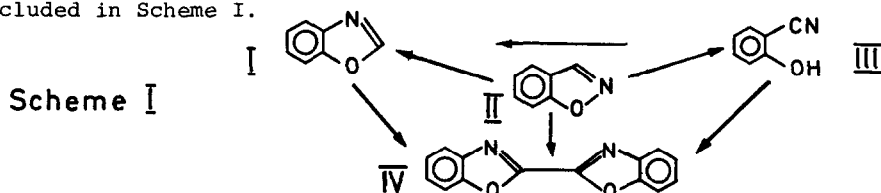
SYMMETRIC PHOTODEHYDRODIMERIZATIONS
FORMATION OF 2,2'-DIBENZOXAZOLE AND 2,2'-DIBENZTHIAZOLE

K. H. Grellmann and E. Tauer
Max-Planck-Institut für Biophysikalische Chemie
Abt. Spektroskopie, D 34 Goettingen, Germany

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Recently, the asymmetric photodehydrodimerization of benzimidazole in solution to 2,5'- and 2,6'-dibenzimidazole has been reported (1). The formation of the symmetric 2,2'-dibenzimidazole was not observed.

We wish to report the symmetric photodehydrodimerization of benzoxazole (I), benzisoxazole (II), and salicylonitrile (III) to 2,2'-dibenzoxazole (IV). In addition to the dimerization reaction, photoisomerizations take place (2) which are included in Scheme I.



Reaction I \rightarrow IV: A solution of 0.5 g I in 500 ml 95% air-saturated ethanol was illuminated for 2 hrs with three 30 W mercury resonance lamps. Part of the product IV already precipitates during the reaction. After evaporation of the solvent and recrystallisation from ethanol IV is obtained in about 90% chemical yield. It is easily identified by its absorption peaks at 340, 322, and 312 (shoulder) nm. A mixed melting point with an authentic sample (3) showed no depression. The reaction takes also place in water, acetonitrile, propanol-1, and butanol-1; in the latter two alcohols with lower quantum yield. The presence of oxygen is essential for the reaction to occur; in degassed solutions IV is not formed. In inert solvents such as methylcyclohexane only traces of IV are observed. Illumination of I at -40° does not yield IV. Instead, another compound is formed, which is presumably 2-isocyanophenol (4). It has a U.V. absorption peak at 288 nm and an I.R. band at 2130 cm^{-1} ($\nu_{\text{N}=\text{C}}$), and decays at room temperature rapidly back to I.

Reaction II \rightarrow IV: The dimer IV was photosynthesized from II similarly to reaction I \rightarrow IV, using an air-saturated solution of 0.4 g/l in acetonitrile. It was identified by its absorption spectrum and mixed melting point (no depression). The solvent dependence is similar to reaction I \rightarrow IV and depends also on the presence of oxygen in the solution. In degassed absolute alcohols salicylaldehyde

or the condensation product trihydroxy hydrobenzamide (5) is - besides I and III - formed (6), which hydrolyse to salicylaldehyd in the presence of water. The chemical yield of $II \longrightarrow IV$ is only about 30%, due to the competing reactions $II \longrightarrow I + III$. The dimer formation occurs directly; the possibility of an indirect reaction $II \longrightarrow I \longrightarrow IV$ can be ruled out by means of selective excitation of II with appropriate filters, since the absorption spectrum of II does not overlap with that of I in the long wavelength region above 280 nm. The other possible indirect route $II \longrightarrow III \longrightarrow IV$ cannot be excluded by selective excitation. However, the quantum yield for the reaction $II \longrightarrow IV$ is about 100 fold greater then for $III \longrightarrow IV$. Therefore, the fraction of indirect formation is negligible.

Reaction III \longrightarrow IV: The dehydrodimerization of III has been demonstrated only spectrophotometrically in diluted (10^{-4} M) airsaturated aqueous, methanolic, and ethanolic solutions, using the characteristic U.V. absorption peaks for identification. The reaction does not take place in acetonitril or methylcyclohexane. In degassed absolute alcohol III forms, similar to II, salicylaldimine (6).

Formation of 2,2'-dibenzthiazole from benzthiazole: This reaction occurs with about 30% chemical yield in airsaturated acetonitrile, but not in methanol, ethanol, propanol-2, water, or methylcyclohexane. Other reactions, which are under investigation, take place in the latter solvents. The dimer was identified by comparison with an authentic sample (mixed melting point, U.V. spectrum).

The mechanisms of the above reactions appear to be rather complex. The quantum yields depend strongly on solvent composition, its pH-value, water content, and oxygen concentration, and are also a function of illumination time. Therefore, standardized conditions have to be established first, in order to investigate quantitatively the dependence of quantum yields on light intensity and educt concentration. So far it is only established that low light intensities and high educt concentrations reduce the quantum yield of dimerisation drastically. Since only few photodimerisations have been reported in the literature (7), the above reactions merit further investigation.

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