Photo-oxidation of Disodium 4,4'-Diacetamidostilbene-2,2'-disulphonate

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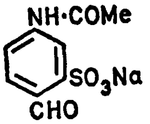
Summary The major product of the photo-oxidation of a stilbene-type fluorescent brightener is identified as sodium 5-acetamido-2-formylbenzenesulphonate.

In our investigation into the mechanism of photosensitization of wool by stilbene-type fluorescent brighteners, we have studied the photo-oxidation of the stilbene-disulphonate (I) in aqueous solution under u.v. light, and determined the structure of the resulting photoproduct. Previous studies concerning the photoreaction of stilbene fluorescent brighteners in solution have attributed the loss of fluorescence to *trans–cis* photoisomerization of these stilbenes.[1,2] More specifically Drefahl and Koellner[2] have attributed changes in the u.v. spectrum of (I) during photolysis to *trans–cis*-photoisomerization. Our present investigation indicates that the observed change is due to cleavage of (I), rather than to *trans–cis*-isomerization.



(II)

The photo-oxidation was carried out as follows. A dilute aqueous solution[3] of (I) (6·7—0·7 × 10^{-3}M; 28 °C) was irradiated with a 100 W, Hanovia high-pressure mercury vapour lamp through a quartz immersion well fitted with a 2-mm Pyrex filter to eliminate > 95% of the light emitted below 300 nm). The photoreaction was followed spectrophotometrically. The resulting solution was evaporated to dryness, and the hygroscopic product was purified by repeated precipitation from aqueous ethanol. It was identified as sodium 5-acetamido-2-formylbenzenesulphonate (II) based on its chemical and spectral properties. Permanganate oxidation of (I) further confirmed the structure of (II).

In the solid state or in solution, especially in the presence of moisture, (I) is photochromic owing to the formation of a charge-transfer complex with oxygen under the influence of u.v. light.[4] However, under the conditions of our experiments, (I) was readily oxidized at the ethylene linkage of the stilbene fragment by dissolved oxygen to give the aldehyde (II). Higher concentrations of oxygen are found to accelerate this oxidation, and oxidation of (I) does not follow a simple kinetic order.

Since photoisomerization of (I) is a distinct possibility, the charge-transfer complex would serve as an ideal precursor for the proposed dioxetan intermediate which subsequently leads to the product. Dioxetans have been shown conclusively to be responsible for the formation of aldehydes in the dye-sensitized photo-oxidation of olefins.[5] They also are found as intermediates in many well known chemiluminescent reactions,[6] as well as in some thermal reactions.[7] Therefore, it is highly probable that dioxetan is an intermediate in this reaction.

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