Nucleophilic Photo-substitution Reaction of Sodium 1-Amino-4-bromoanthraquinone-2-sulphonate

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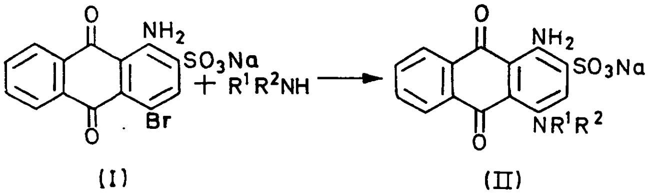
Summary Sodium 1-amino-4-bromoanthraquinone-2-sulphonate is photo-aminated to form sodium 1-amino-4-alkylaminoanthraquinone-2-sulphonate with ammonia or alkylamines in aerated aqueous alcohol.

THE photochemistry of quinone derivatives has attracted much attention in relation to the phototendering effect of vat dyes, and many studies concerning photo-reduction and photo-annelation have been made.[1] However, photo-substitution reactions of quinones have not previously been reported.

We report that the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulphonate (I) occurs in aqueous alcohol in the presence of ammonia or alkylamines.



(I) (II)

$\mathrm{R^1R^2NH = NH_3, MeNH_2, EtNH_2, Pr^nNH_2, Bu^nNH_2}$, piperidine. Wavelength > 300 nm.

Solutions of (I) and ammonia of alkylamine in aerated 4:1 alcohol–water were irradiated using a high-pressure Hg lamp with a glass filter. In each case, the photo-reaction of (I) with ammonia or alkylamine gave only one aminated product (II), which was identified by comparison with an authentic sample. The effect of the solvent on the reaction is shown in the Table. The reactions were promoted by the presence of alcohol and acetonitrile. The reactions did not proceed under nitrogen, with or without $\mathrm{Fe^{3+}}$ as oxidizing agent.[2] When irradiation was carried out without filtering-out the u.v. radiation, the substitution reaction did not occur, but the intensity of the first absorption band of (I) ($\lambda_{\max}$ 490 nm) decreased. When the radiation from the Hg lamp was filtered with a V-Y-42 filter (Toshiba) which allows through only radiation of $\lambda > 420$ nm, the substitution reaction took place. No dark reaction was observed under the same conditions.

TABLE

The effect of the solvent on the yield of aminated product (II)

Solvent	Yield (%)
Water	11·7
4:1 Methanol–water	41·7
4:1 Ethanol–water	44·3
4:1 Propan-1-ol–water	39·3
4:1 Propan-2-ol–water	48·6
4:1 t-Butyl alcohol–water	39·3
4:1 Acetonitrile–water	54·7
4:1 Dioxan–water	23·4

[I] *ca.* $0{\cdot}990 \times 10^{-4}$ M; $[\mathrm{NH_3}]$ *ca.* $4{\cdot}37 \times 10^{-2}$ M; irradiation time 8 h.

When the reaction was carried out without amine and in the presence of alkali (*ca.* $4{\cdot}84 \times 10^{-2}$ M), the absorption intensity at 490 nm only decreased slightly When aromatic amines such as aniline and diphenylamine were used, the substitution reaction did not occur and (I) remained unchanged, both under nitrogen and under air

These results show that the substitution reaction of (I) with ammonia or alkylamine is induced by the absorption of light corresponding to the first absorption band of (I), and the reaction is greatly affected by the properties of the solvents (polarity and ability to form hydrogen bonds) and by the presence of oxygen

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[1] J M Bruce, *Quart Rev* , 1967, **21**, 405

[2] N K Bridge and M Reed, *Trans Faraday Soc* , 1960, **56**, 1796