# Photochemical Syntheses of Aminoanthraquinone Sulphonates

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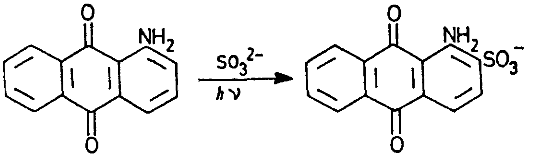
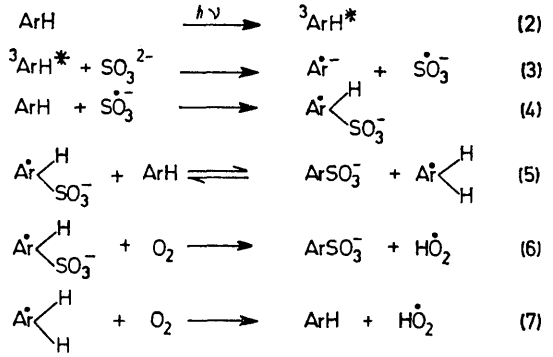
*Summary* Irradiation of 1-aminoanthraquinone and sodium sulphite in aqueous pyridine with visible light results in the formation of sodium 1-aminoanthraquinone-2-sulphonate in 92·6% yield; other aminoanthraquinone sulphonates may be similarly prepared.

The photochemical syntheses of amino-, chloro-, and hydroxy-anthraquinones from reactions which involve the replacement of the $NaSO_3$ group,[1] OMe,[2] or bromine[3] by the appropriate substituent have attracted considerable attention recently. However, related syntheses which involve the replacement of aromatic hydrogen by electronegative groups in alkaline solution have received less attention partly because of the complex product mixtures usually produced in this type of reaction. For example, the photochemical hydroxylation of sodium anthraquinone-2-sulphonate leads to the formation of at least six hydroxylated products.[4]


(1)

A preliminary study of the photochemical reactions of 1- and 2-aminoanthraquinones and some of their derivatives with the sulphite anion in alkaline solution has shown that aminoanthraquinone sulphonates may be synthesised in high yield by direct replacement of aromatic hydrogen. Reactions were carried out by visible irradiation with an external 400 W high pressure discharge lamp (Thorn Kolorarc) of the appropriate aminoanthraquinone (1·5 mmol) and sodium sulphite (15 mmol) at 23 ± 2 °C for 24 h in 50% aqueous pyridine (400 ml) contained in a glass tube reactor fitted with an external water cooling jacket. The product was identified either by a comparison with an authentic sample or by $^1H$ n.m.r. spectroscopy. Yields were assessed by visible spectroscopy in the 470—500 nm region and the reactions were monitored by t.l.c. on aluminium sheets (Merck) precoated with Silica Gel 60 $F_{254}$ using dioxan–n-butanol–ammonia–water (4 : 2 : 1 : 1) as eluant.



1-Aminoanthraquinone gives sodium 1-aminoanthraquinone-2-sulphonate exclusively under the specified conditions in 92·6% yield and 75·2% conversion, as shown in equation 1.† No dark reaction is observed under the same conditions. The photosubstitution proceeds under air or with nitrogen saturated solutions. With oxygenated solutions, however, conversions are poor because of the oxidation of the sulphite anion to sulphate. The reaction is not inhibited by the presence of one or more halogen substituents in the 4-, 5-, 6-, 7-, or 8-positions of the amino-compound. Thus, 1-amino-4-chloroanthraquinone gives sodium 1-amino-4-chloroanthraquinone-2-sulphonate in 100% yield and 94·7% conversion under the specified conditions. Similarly, 1-amino-5-chloroanthraquinone gives sodium 1-amino-5-chloroanthraquinone-2-sulphonate in 96·5% yield and 85·4% conversion. When the *ortho*-position to the amino- group is blocked, however, little or

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† Yield is based on the proportion of substrate consumed.

no reaction occurs at the 4-position of the molecule. Thus, 97% of 1-amino-2-methylanthraquinone is recovered unchanged after irradiation under the specified conditions.

The reactions are believed to proceed by the formation of the sulphite radical anion, and its subsequent reaction with the substrate to form an adduct[5] which on oxidation gives the product, as shown in equations 2—7. The same radical anion is almost certainly generated in the related thermal dark reaction of 1-aminoanthraquinone which also proceeds with high selectivity to give the 2-sulphonate.[6] The remarkable selectivity of the sulphite radical anion for the electron-rich 2-position of the 1-aminoanthraquinone[7] probably reflects an early transition state for this type of substitution reaction.

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[1] A. V. El'tsov, O. P. Studzinskii, O. V. Kul'bitskaya, N. V. Ogol'tsova, and L. S. Efros, *Zhur. org. Khim.*, 1970, **6**, 638; A. V. El'tsov, O. P. Studzinskii, and N. I. Ttishchev, *ibid.*, 1971, **7**, 1272; 1972, **8**, 349 and 774; 1973, **9**, 740; G. G. Wubbels, D. M. Tollefson, R. S. Meredith, and L. A. Herwaldt, *J. Amer. Chem. Soc.*, 1973, **95**, 3820.

[2] J. Griffiths and C. Hawkins, *J.C.S. Perkin I*, 1974, 2283.

[3] H. Inoue, T. D. Tuong, M. Hida, and T. Murata, *Chem. Comm.*, 1971, 1347.

[4] A. D. Broadbent and R. P. Newton, *Canad. J. Chem.*, 1972, **50**, 381.

[5] J. O. Morley, *J.C.S. Perkin II*, 1973, 1626.

[6] J. O. Morley, B. P. Application 16876, 1973 (to I.C.I. Ltd.).

[7] J. O. Morley, *J.C.S. Perkin II*, 1972, 1223.