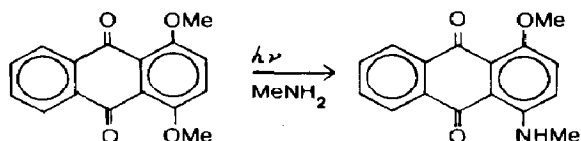


Organic Photochemical Synthesis

1-Methoxy-4-methylamino-9,10-anthraquinone



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1. Procedure

The apparatus consists of a 1.5 l flask fitted with a thermometer and an efficient water-cooled cold-finger and with provision for magnetic stirring. Two 300 W tungsten filament lamps (note 1) are placed at opposite sides of the flask at a distance of 2 - 3 cm from the flask wall.

A 33% ethanolic solution of methylamine (80 ml) is added to a solution of 1,4-dimethoxy-9,10-anthraquinone (note 2) (2.68 g, 0.01 mol) in dichloromethane (1300 ml). The mixture is stirred and irradiated for approximately 13 h (note 3), maintaining the temperature in the range 20 - 25 °C. The initially orange solution becomes deep purple. The solvent and excess amine are removed on a rotary evaporator, and the residue is dissolved in dichloromethane (300 ml). The solution is extracted with concentrated hydrochloric acid (2 × 100 ml). Evaporation of the dichloromethane solution, after drying over anhydrous magnesium sulphate, gives the starting material (0.6 g, 22%). The acid extracts are diluted to a total volume of 1600 ml with water and extracted rigorously with dichloromethane until no more coloured material remains in the aqueous layer. The combined extracts are washed until neutral and dried over anhydrous magnesium sulphate. Evaporation of the filtered extracts gives 1-methoxy-4-methylamino-9,10-anthraquinone as a dark purple solid (melting point, 164 - 165 °C (162 - 163 °C reported in ref. 1)). The yield is 1.9 g (71%) (note 4).

2. Notes

(1) The reaction proceeds best with radiation in the 350 - 450 nm range. A medium pressure mercury lamp may be used in conjunction with a Pyrex vessel, but secondary decomposition of the product is then more significant.

(2) The starting material (melting point, 170 - 171 °C) is prepared most conveniently by methylation of quinizarin (1,4-dihydroxy-9,10-anthraqui-

none) with methyl *p*-toluenesulphonate in trichlorobenzene at 160 - 170 °C in the presence of sodium carbonate [2].

(3) As the product absorbs to a significant extent in the active part of the spectrum (350 - 450 nm), the reaction rate diminishes markedly at high conversions. Under the conditions described, conversions greater than about 80% are impractical, and, particularly in view of the ease of separating starting material and product, lower conversions are generally more convenient.

(4) The yield is dependent on the exposure time and the type of radiation source used (see note 1). With tungsten filament lamps the yield, based on converted starting material, is generally better than 90%.

3. Methods of preparation

1-Methoxy-4-methylamino-9,10-anthraquinone has been prepared by heating 1-bromo-4-methylamino-9,10-anthraquinone with sodium methoxide, sodium acetate and cupric acetate in methanol at 85 °C in an autoclave [3]. It has also been prepared by heating 1-methoxy-4-chloro-9,10-anthraquinone with *N*-methyl-*p*-toluenesulphonamide, potassium carbonate, cupric carbonate and copper powder in nitrobenzene at 170 - 180 °C, followed by hydrolysis of the product with concentrated sulphuric acid [1].

4. Merits of the preparation

The procedure described here provides a milder and more efficient route to 1-methoxy-4-methylamino-9,10-anthraquinone than do conventional thermal nucleophilic substitution procedures. In addition the starting material is more readily available than those generally required for the thermal routes.

The procedure is one example illustrating the reactivity of methoxy-substituted quinone systems towards photochemical nucleophilic substitution. In the present case methylamine can be replaced by ammonia, any primary alkylamine or cycloalkylamine, but the reaction does not proceed with secondary amines or primary arylamines. The photochemical procedure is thus particularly suited to the synthesis of 1-amino-4-methoxy-9,10-anthraquinones where the volatility or thermal sensitivity of the amine used would pose experimental difficulties with thermal substitution procedures. In addition the photochemical reactions are highly selective and, once one amino group is introduced, the quinone system is deactivated towards further substitution. In thermal procedures the bis-substituted compounds are often formed in significant amounts. Methoxyl groups show a generally high photochemical lability in quinonoid systems, which can often be of value in the synthesis of amino-substituted derivatives. Thus 1- and 2-methoxy-9,10-anthraquinone [4], 5-methoxy- and 5,8-dimethoxy-1,4-naphthoquinone [5] and various heterocyclic methoxy-substituted quinones [6] react readily with amines on exposure to near-UV radiation.

- 1 K. Naiki, *J. Soc. Org. Synth. Chem. Jpn.*, **13** (1955) 5140; *Chem. Abstracts*, **51** (1957), no. 1612.
- 2 K. Zahn and P. Ochwat, *Justus Liebigs Ann. Chem.*, **462** (1928) 95.
- 3 F. Bayer and Company, *Ger. Patent 229,316*, 1910.
- 4 J. Griffiths and C. Hawkins, *J. Chem. Soc., Perkin Trans. I*, (1974) 2283.
- 5 K. Y. Chu and J. Griffiths, *J. Chem. Res. (S)*, (1978) 180; *J. Chem. Res. (M)*, (1978) 2319.
- 6 G. Green-Buckley and J. Griffiths, *J. Chem. Soc., Chem. Commun.*, (1977) 396; *J. Chem. Soc., Perkin Trans. I*, (1979) 702.

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