Regiospecific Attack of Methoxide Ion on 4-Alkoxy-*o*-quinone Imines. A Novel Route to *p*-Quinone Monoacetals

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Summary In the solvolysis of 4-alkoxy-5-methyl-*o*-benzoquinone *N*-arylsulphonylimines (**1a**) and (**1b**) (NaOH–MeOH–H_2O), the regiospecific attack of MeO^- occurs initially on the carbon atom substituted by the alkoxy-group to produce the *p*-benzoquinone monoacetals (**3a**) and (**3b**), respectively.

p-QUINONE MONACETALS are useful synthetic intermediates[1] and are prepared by partial hydrolysis of the corresponding bisacetals[2] or by oxidation of *p*-alkoxyphenols in the presence of alcohols.[3] This paper describes the solvolysis of 4-alkoxy-*o*-benzoquinone *N*-sulphonylimines and a new route for the preparation of amido-substituted *p*-quinone monoacetals.

The methoxy- and hexadecyloxy-quinone imines (**1a**) (m.p. 138—148 °C)† and (**1b**) (m.p. 90—91 °C),† respectively, were synthesized by oxidation of the corresponding phenols (**2a**) and (**2b**) with manganese dioxide. A solution of (**1a**) (0·5 g) in methanol (50 ml) was treated with 1N aqueous sodium hydroxide (2·5 ml) and the mixture stirred for 5 min. Quenching with acetic acid and work-up gave an acid-labile product (**3a**) (m.p. 101—104 °C) whose mass

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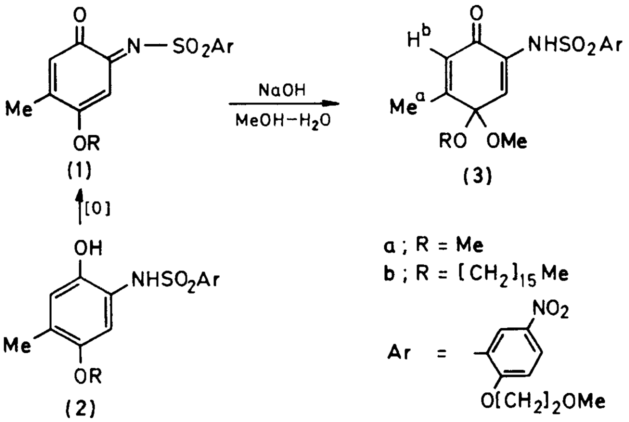
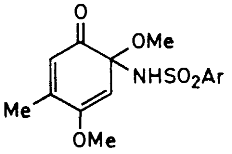
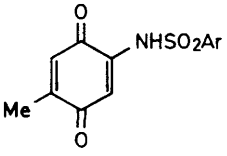
† All new compounds gave correct elemental analyses.

spectral (*m/e* 442)‡ and analytical data† were in agreement with a methanol adduct. The ^{1}H n.m.r. spectrum§ of (**3a**) exhibited a singlet (6H) at δ 3·10 (2 × OMe), and the long-range coupling constant (J 2 Hz) between Me^a (δ 1·90) and H^b (δ 6·10) was very similar to that for cross-conjugated dienones (1·6 Hz).[4] Moreover, the presence of a sulphonamide group in (**3a**) was shown by its ^{1}H n.m.r. (δ 7·99, br.) and i.r. spectra (ν_{max} 3380 cm^{-1}, Nujol mull). These data showed that the methanol adduct had the *p*-quinone monoacetal structure (**3a**) and excluded the alternative conjugated dienone structure (**4**).

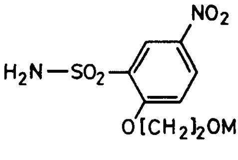




(**4**)



(**6**)



(**5**)

Similarly, the methanol adduct (**3b**)† (m.p. 41—44 °C; *m/e* 652)‡ was obtained by solvolysis of (**1b**). The ^{1}H n.m.r. signal§ of the 4-methoxy-group of (**3b**) appeared at δ 3·06, which was in the same region as that for (**3a**). The mixed monoacetal structure of (**3b**) was interesting because it showed less steric hindrance than similar compounds.[3a]

'Ballasted' *o*-sulphonylaminophenols (**2**), wherein R is a hexadecyl group and Ar is a dye moiety, have been proposed as dye-releasing redox compounds in diffusion-transfer (so-called 'instant') photography.[5]¶ They have been presumed to undergo imagewise oxidation during photographic developing processes to afford *o*-quinone *N*-sulphonylimines (**1**), which are subsequently hydrolysed to diffusible dyes. In order to clarify the dye-releasing mechanisms, the reaction of (**1b**) with methanolic sodium hydroxide was followed as a function of time. At first, the adduct (**3b**) was detected in 94% yield and then gradually disappeared, to be replaced by the adduct (**3a**) whose concentration rose to a maximum and then diminished. As the amounts of (**3b**) and (**3a**) decreased, 2-(2-methoxyethoxy)-5-nitrobenzenesulphonamide (**5**) (a model compound for diffusible dyes) was increasingly formed.

Acidic hydrolysis of (**1a**) or (**1b**) proceeded differently to provide the quinone (**6**) (m.p. 149—151 °C).† These results contrast sharply with those for *p*-benzoquinone *N*-sulphonylimines, which have been reported to give the corresponding *p*-arylsulphonylaminophenols under basic conditions[6a] and to afford *p*-benzoquinone and arenesulphonamide under acidic conditions.[6b]

In summary, our experiments strongly suggest that a nucleophilic reagent attacks initially at the carbon atom substituted by the alkoxy-group rather than at the 2-imine carbon atom of the quinone imines.

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‡ Determined by field-desorption mass spectrometry.

§ ^{1}H N.m.r. spectra were determined in CDCl$_3$ solutions at 90 MHz.

¶ The term 'ballasted' is widely used in photographic chemistry and means non-diffusible or immobile. In compound (**2b**) the hexadecyloxy-group is called a 'ballast' group.

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