Photochemical Nucleophilic Substitution of Simple Anthraquinone Derivatives

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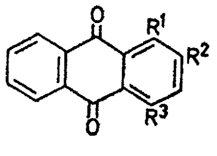
Summary 1- and 2-Methoxyanthraquinone undergo rapid photochemical nucleophilic substitution by ammonia in solution, quenching and sensitisation studies suggesting the involvement of the first excited (π,π^*) or (n,π^*) singlet states of the anthraquinone.

Photochemically-induced nucleophilic substitution of simple aromatic compounds has received considerable attention. In contrast, anthraquinone derivatives have been relatively neglected, although nucleophilic substitution reactions are characteristic of their ground-state chemistry. Recent studies have shown that anthraquinone sulphonic acids will react photochemically with aqueous alkali,[1] water,[2] chloride ions, and ammonia,[3] but in view of the complexity of the products and the retarding effect of radical scavengers, these cannot be regarded as simple nucleophilic displacement reactions. The displacement of bromine from 1-amino-4-bromoanthraquinone-2-sulphonic acid by amines on exposure to light has been reported,[4] but again the reaction appears to be relatively complex in that oxygen is essential for the substitution to occur. With simple benzene derivatives, photochemical nucleophilic substitution is particularly favoured by the presence of a powerful electron-withdrawing group (*e.g.* NO_2) with a good leaving group (*e.g.* OMe) in the *meta* position.[5] To explore the possibility of photochemical nucleophilic substitution in anthraquinones, the derivatives 1-methoxy- (I) and 2-methoxy- (II) anthraquinone were examined, using ammonia as the nucleophile. In both compounds the methoxy-groups are *meta* to one of the quinone carbonyl groups.

Solutions (2×10^{-3}M) of 1-methoxyanthraquinone in 1 : 1 water–acetonitrile rapidly reacted with dissolved ammonia (7M) when exposed to Pyrex-filtered u.v. light. The products were isolated by chromatography over silica gel, and were identified by m.p., i.r., and g.l.c. comparison with authentic samples as 1-aminoanthraquinone (III) and 1-amino-4-methoxyanthraquinone (IV), in yields of 96 and *ca.* 0·5%, respectively.† Under identical conditions 2-methoxyanthraquinone reacted less rapidly to give 2-aminoanthraquinone (V) (25%) and 1-amino-2-methoxyanthraquinone (VI) (70%). The reactions were remarkably clean, and proceeded smoothly under air or nitrogen.



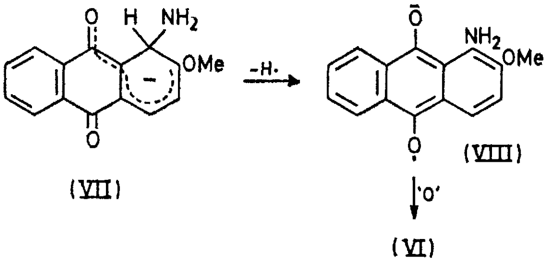
(I) R^1 = OMe, R^2 = R^3 = H
(II) R^1 = R^3 = H, R^2 = OMe
(III) R^1 = NH_2, R^2 = R^3 = H
(IV) R^1 = OMe, R^2 = H, R^3 = NH_2
(V) R^1 = R^3 = H, R^2 = NH_2
(VI) R^1 = NH_2, R^2 = OMe, R^3 = H

To evaluate the possible involvement of radical intermediates in these reactions, solutions were irradiated in the presence of the radical scavenger 2,6-di-t-butylphenol. The rate of reaction of (I) with ammonia was unaffected, whereas the rate was actually increased in the case of (II). In the latter reaction the rate of formation of (V) was unaffected, but the rate of formation of (VI) increased significantly. Although this observation requires further explanation, both results discount radical substitution mechanisms.

† Yields were calculated by g.l.c. analysis, using a 5 ft. column of 10% E30 on siliconised diatomite C at 242°.

Photochemical excitation of (I) produces an excited state in which there is presumably a decrease in charge density at position 1, enabling attack by ammonia to occur to give an intermediate negatively charged σ-complex (ground or excited state). Loss of methoxide from this then leads to (III) in the usual way. In the case of (II) a similar, though less favourable, attack at position 2 by ammonia leads to the formation of (V). However, it appears that in the excited state of (II) the alternative attack at position 1 is favoured over attack at position 2, even though the intermediate σ-complex (VII) cannot easily eliminate hydride ion to give the substitution product. Formation of (VI) could occur more easily by homolytic loss of hydrogen from (VII), giving the relatively stable semiquinone radical (VIII), which can then be oxidised to (VI). Oxygen should thus favour this reaction, and in agreement with this it was found that the rate of formation of (VI) was reduced drastically in the absence of oxygen, although the rate of formation of (V) was unaffected.

To provide further information about the nature of the excited states involved in these reactions, triplet sensitisation and quenching experiments were carried out. Both 1-methoxy- and 2-methoxy-anthraquinone have superimposed lowest (π,π^*) and (n,π^*) singlet excited states of energy *ca.* 60 kcal mol^{-1}. In the presence of fluorenone (E_T 53 kcal mol^{-1}), which should be capable of sensitising the lowest triplet states, the substitution reactions of (I) and (II) were inhibited. The triplet quencher piperylene (E_T 55 kcal mol^{-1}) had no retarding effect on the reactions, and thus it appears that photosubstitution occurs from a lowest excited singlet state, although it is not possible to evaluate the relative roles of the (π,π^*) and (n,π^*) singlet states. The possibility that a vibrationally excited level of the ground state is involved appears to be unlikely, since (IV) and (VI) are not formed in the thermal reactions of (I) and (II) with ammonia.



These results appear to be the first examples of simple photochemical nucleophilic substitution in anthraquinones. The efficiency and specificity of the reactions indicate that reactions of this type could be of general preparative value in anthraquinone chemistry.

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