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# Reagent Influence on the Direction of Nucleophilic Substitution in 1,4-Nitrochloroanthraquinone

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In the reaction of 1,4-nitrochloroanthraquinone with phenoxy anions in DMSO, the main products are those of chlorine substitution, whereas thiophenoxy anions predominantly replace the nitro group.

The chlorine atom of nitrochloro-substituted aromatic compounds, when occupying a conjugate position relative to the $NO_2$ group, has a significantly higher mobility in $S_NAr$ reactions than the latter, being practically the only atom attacked by different nucleophiles.[1,2] However, under certain circumstances, the rates of substitution of both functions in nitrochloroarenes became comparable either due to the increased ability of the $NO_2$ group to be substituted or due to the decreased mobility of the chlorine atom. For example, steric hindrance to location of the nitro group in the aromatic ring plane leads to an inability of the group to fully stabilize the intermediate σ-complexes of chlorine substitution.[3–5] Otherwise, the mobility of the $NO_2$ group activating chlorine substitution increases in its turn under the influence of a third substituent,[6,7] or both factors work at once.[8] With comparable mobility of the chlorine atom and the nitro group, the predominant direction of nucleophilic attack may be determined by the properties of the nucleophile, in particular, by the ratio of contributions of electrostatic and orbital terms into the energy of interaction with a substrate.[9–11]

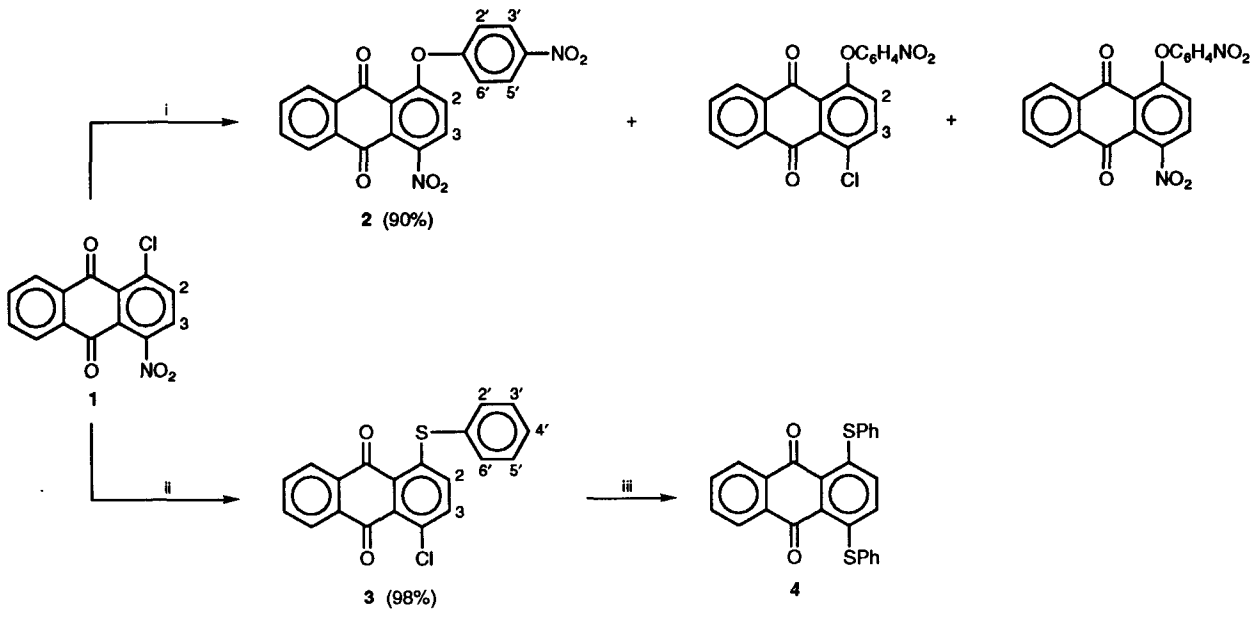
We have shown that the nature of the electron-donating atom in the nucleophile is a factor capable of changing the predominant direction of substitution in 1,4-nitrochloroanthraquinone **1**, where the influence of the nitro group is weaker because of its non-coplanar position, but both substituents are activated to $S_NAr$ reactions by the adjacent carbonyl groups. Nucleophilic substitution in substrate **1** has previously been investigated only for its reactions with amines replacing both the chlorine atom and the $NO_2$ group.[12,13]

The nucleophiles chosen by us, the 4-nitrophenoxy and thiophenoxy anions (as sodium salts), are characterized by approximately the same basicities (the $pK_a$ values of conjugated acids in DMSO are 10.8 and 10.3, respectively[14]) and very different polarizability, *i.e.*, the 'softness'.

The interaction of substrate **1** with an equimolar amount of 4-nitrophenoxide in DMSO is rather sluggish, but after 7 h at 70 °C the conversion degree was 89%, 90% of the product† being 4-nitro-1-(4′-nitrophenoxy)anthraquinone **2**.‡ The product of nitro group substitution was formed only in trace

† The composition of the reaction mixtures was established by chromatographic separation and by LC data.

‡ 4-Nitro-1-(4′-nitrophenoxy)anthraquinone **2**, m.p. 209–210 °C, $^1$H NMR ($CDCl_3$) 7.07 (2H, d, *J* 9.0 Hz, H-2′, H-6′), 7.53 (d, *J* 9.0 Hz, H-2), 7.79 (d, *J* 9.0 Hz, H-3), 7.72–7.88 (2H, m, H-6, H-7), 8.09–8.29 (2H, m, H-5, H-8), 8.25 (2H, d, *J*, 9.0 Hz, H-3′, H-5′); *m/z* Found/Calc. 390.0486/390.0488.



**Scheme 1** *Reagents and conditions*: i, $4\text{-}NO_2C_6H_4O^-Na^+$, 70 °C, 7 h; ii, $PhS^-Na^+$, 25 °C, 30 s; iii, $PhS^-Na^+$, 25 °C, 30 min.

amounts and was not isolated individually. Heavily predominant chlorine substitution was also observed by us for the more basic phenoxy, 4-bromophenoxy and 2-naphthoxy anions. In all cases at an equimolar ratio of reagents, the products of $NO_2$ substitution were obtained in far less significant quantities, as well as 1,4-bis(aryloxy)anthraquinones formed by replacement of both substituents. Compound **1** reacts with 1 mol of sodium thiophenoxide almost completely during 30 s at room temperature, the only product being 1-phenylmercapto-4-chloroanthraquinone **3**.§ The reaction of compound **1** with 2 mol of the thiophenoxide during 30 min at room temperature leads to a mixture of **3** with a product of substitution of both functions, *i.e.* 1,4-bis(phenylmercapto)anthraquinone **4**.¶ Product **4** was also obtained in high yield by the reaction of compound **3** with a thiophenoxide salt. The predominant formation of the product of nitro group substitution in compound **1** was also observed in the reaction of **1** with the 4-nitrothiophenoxy anion.

Thus, the predominant direction of nucleophilic substitution at one of the two reaction C-centres in **1** changes on passing from hard O-anions to the soft, easily polarizable S-anions. It follows from MNDO calculations that in the derivative of anthraquinone **1** (in contrast, *e.g.*, to 4-chloronitrobenzene), the orbital of the C-atom bonded to the $NO_2$ group makes an appreciably greater contribution to the LUMO, which favours the attack of this position by S-anions. At the same time, due to the presence of a small positive charge on the carbon bonded to chlorine, the hard O-anions react specifically with this carbon atom.

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§ 4-Chloro-1-phenylmercaptoanthraquinone **3**, m.p. 165–168 °C, $^1H$ NMR ($CDCl_3$) 6.96 (d, *J* 9.0 Hz, H-2), 7.35 (d, *J* 9.0 Hz, H-3), 7.44–7.52 (3H, m, H-2′, H-4′, H-6′), 7.57–7.64 (2H, m, H-3′, H-5′), 7.73–7.83 (2H, m, H-6, H-7), 8.19–8.34 (2H, m, H-5, H-8); *m/z* Found/Calc. 350.0163/350.0168.

¶ 1,4-Bis(phenylmercapto)anthraquinone **4**, m.p. 235–239 °C, $^1H$ NMR, ($CDCl_3$), 6.78 (2H, s, H-2, H-3), 7.38–7.46 (6H, m, H-2′, H-4′, H-6′), 7.52–7.59 (4H, m, H-3′, H-5′), 7.76–7.86 (2H, m, H-6, H-7), 8.30–8.43 (2H, m, H-5, H-8); Found/Calc. *m/z* 424.0595/424.0592.

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