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ELECTROCHEMICAL OXIDATIVE SUBSTITUTION AND DIMERISATION OF 1-ARYLAZO-2-NAPHTHOLS, LEADING TO A NEW SYNTHESIS OF SOME UNSYMMETRICAL DIARYLAMINES

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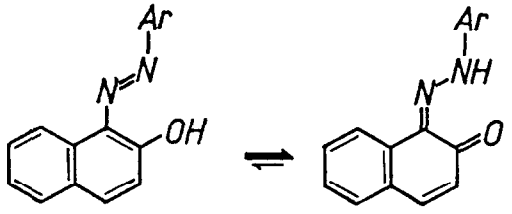
Abstract. Some electron-rich 1-arylazo-2-naphthols undergo novel electrochemical oxidations, leading either to substitution by a nucleophilic aniline or to oxidative dimerisation. In the former case subsequent reduction of the azo bond provides a new route to unsymmetrical diarylamines.

The electrochemical reduction of arylazo compounds is well-known.[1] The corresponding oxidation of these species is far less-well documented.[2] In the course of attempts to synthesise novel heterocyclic compounds by electrooxidative routes, we have electrolysed solutions of the arylazo compounds, (1). In the event, no cyclised products based on (1) have yet been observed. However, two new oxidative reactions have been discovered, which may have synthetic potential.

Available evidence[3] indicates that (1) exists in solution predominantly as the hydrazo tautomer (2), so that both (1) and (2) are potential substrates for electrolysis.

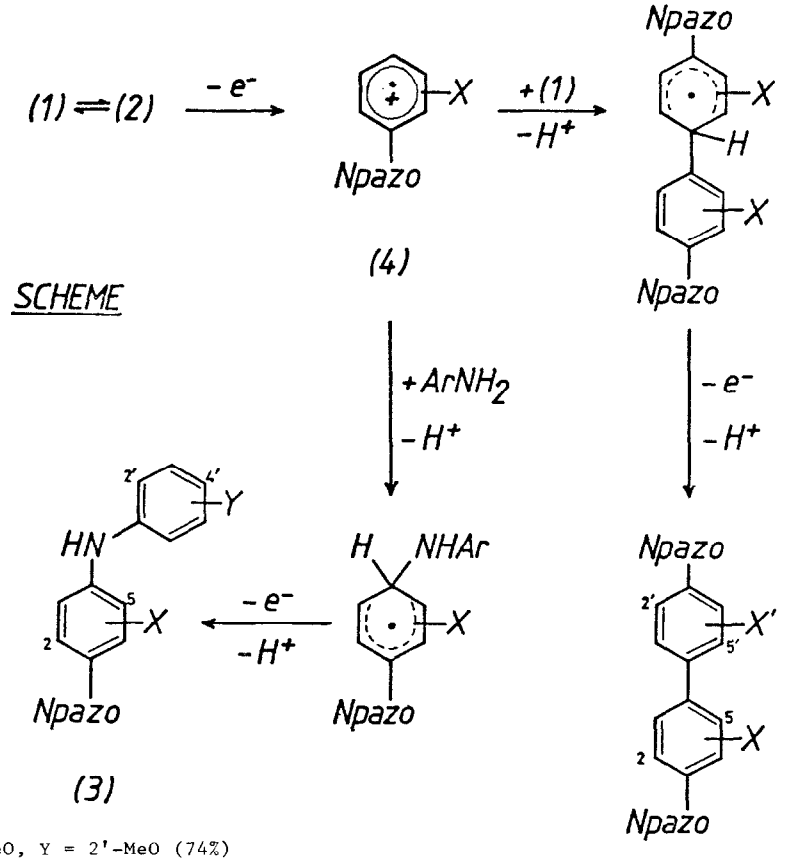


(1) (2)

(a) Ar = 2-$MeOC_6H_4$
(b) Ar = 2,5-$(MeO)_2C_6H_3$
(c) Ar = 2-MeO-5-MeC_6H_3
(d) Ar = C_6H_5
(e) Ar = 2-MeC_6H_4
(f) Ar = 3-$MeOC_6H_4$
(g) Ar = 4-$MeOC_6H_4$
(h) Ar = 4-MeC_6H_4

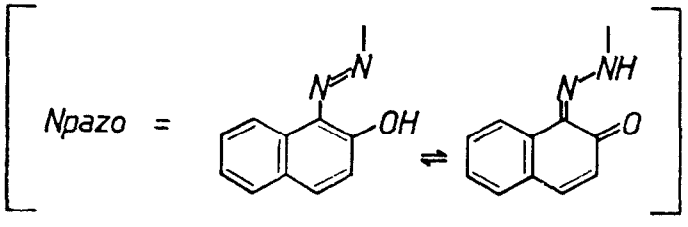
Electrolysis of (1a) in a 2-compartment cell,[4] where transfer of electrolyte between anode and cathode was possible, resulted in production of a new coloured compound, as monitored by tlc and change of colour of the solution. Work-up of the reaction mixture yielded (3a)[5] and 1,2-naphthoquinone. When the electrolysis was repeated in a 3-compartment cell[4] (no transfer of solution between anode and cathode compartments possible), with (1a) confined to the anode compartment, no electrolysis products were observed. However, electrolysis after the addition of o-anisidine to the solution of (1a) in the anode compartment again led to the formation of (3a). If o-anisidine was replaced by p-anisidine, the corresponding isomeric product (3b) could be isolated.

The results of these observations are rationalised as follows. Electroreduction of (1a) occurs at the cathode in the 2-compartment cell to give o-anisidine and 1-amino-2-hydroxy-naphthalene. The latter is oxidised to the observed quinone under the conditions of the experiment.[6] Unreacted (1a) is oxidised at the anode to radical cation (4), where it reacts further with the o-anisidine to give observed product (3a) (Scheme). In the absence of a reductive step (3-compartment cell) no o-anisidine is generated, so formation of (3a) is no longer possible until the anisidine is intentionally added to the anode compartment.



(a) X = 2-MeO, Y = 2'-MeO (74%)
(b) X = 2-MeO, Y = 4'-MeO (7%)
(c) X = 2,5-$(MeO)_2$, Y = 2'-MeO
(d) X = 2,5-$(MeO)_2$, Y = 4'-MeO (28%)
(e) X = 2-MeO-5-Me, Y = 2'-MeO
(f) X = 2-MeO-5-Me, Y = 4'-MeO (9%)

(a) X = 2,5-$(MeO)_2$, X' = 2',5'-$(MeO)_2$ (34%)
(b) X = 2-MeO-5-Me, X' = 2'-MeO-5'-Me (14%)
(c) X = 2,5-$(Me)_2$, X' = 2',5'-$(Me)_2$



Electrooxidation of the 2,5-dimethoxy analogue (1b) in a 3-compartment cell in the absence of free anisidine followed a different pathway. In contrast to the lack of reaction of (1a), the primary oxidised species (4) reacts with unoxidised (1b), and is then further oxidised to the dimeric product (5a) (Scheme). If, however, either o- or p-anisidine are added to the anode compartment, this oxidative dimerisation is suppressed in favour of oxidative substitution to give (3c) and (3d), respectively. Thus, under these conditions, the reaction reverts to that of the analogue (1a). Parallel behaviour is noted for the 2-methoxy-5-methyl derivative (1c), where oxidative dimerisation to (5b) in the absence of added aniline gives way to formation of (3e) or (3f) in the presence of the anisidines. In contrast, the 2,5-dimethyl derivative (1d) preferentially gives the dimer irrespective of the presence or absence of other nucleophilic anilines.

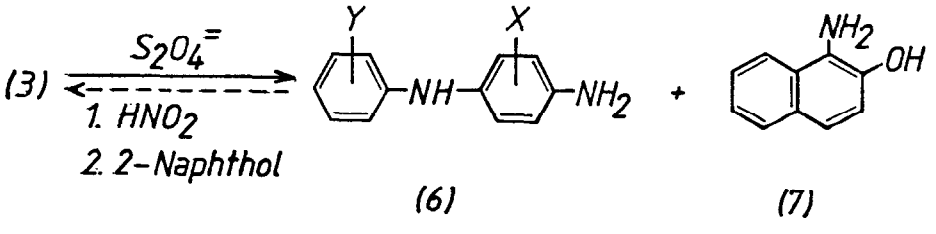
There are several restrictions to the generality of these reactions:

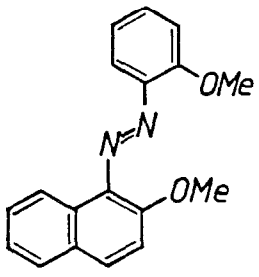
- Relatively electron-rich species favour this electrooxidation. Thus, (1d), which is unsubstituted, (1e), which is substituted by a weakly donating 2-methyl group, and (1f), which contains a less well conjugated donor, give very low yields from electrooxidations (products not isolated).
- Furthermore, (1) must be unsubstituted para to the azo group, since (1g) and (1h) gave no isolable product. Only para-attack in (4) has been observed.
- Apparently, only very nucleophilic or readily oxidised anilines attack (4). m-Anisidine, for example, fails to react with (1a). (An alternative mechanistic rationalisation for production of (3) and (5), compared with that in the Scheme, involves coupling of two cation radicals.)

The yields of the products (3) and (5) are very dependent on the exact conditions used, ranging upwards from 7%. (See Scheme, where yields are unoptimised, but refer to chromatographed, then recrystallised material. Missing data imply the products were not 100% pure.) However, a partially optimised reaction between (1a) and an excess of o-anisidine gave (3a) in 74% yield. Further electrooxidation of the primary products, (3) or (5), is the main obstacle to higher yields.

To date, we have been unable to effect these reactions by chemical oxidants. Nor have we found any report of analogous reactions in the literature.

Some of the arylaminoanilines (6), necessary for direct synthesis of (3) by conventional diazotisation-coupling, are not readily available. Thus the new electrochemical route to (3) has further novel synthetic potential, in that the reaction offers an attractive entry to such unsymmetrical electron-rich diarylamines (6). For instance, dithionite reduction of (3a) gave a quantitative yield of (6; X = 2-MeO, Y = 2'-MeO), along with 1-amino-2-hydroxynaphthalene (7).[7] This degradation also provides further confirmation of the structure of (3a), in addition to physical evidence.[5]





(8)

The oxidised species is believed to be the hydrazo tautomer (2). No arylazo compound known to be constrained in the azo form, including the O-methylated derivative (8),[8] has been oxidised under the conditions we have used for the reactions described in this Letter. This is consistent with the observed oxidative pathway. Electron loss at the anode is expected to be easier for the relatively electron-rich hydrazo-substituted ring in (2) (i.e. donor-substituted), compared with the tautomer (1) which contains the electron-withdrawing azo group. The relative tendency of a substrate to undergo oxidative substitution compared with dimerisation probably depends on the degree and type of molecular association at the anode surface.

Conclusion - These results show that aromatic amines can be protected as arylazo-2-naphthols, and are then activated toward oxidative aromatic substitution selectively at the para-position.

Acknowledgement - We thank the SERC for a CASE award to DJR.

References and footnotes

1. F.G.Thomas and K.G.Boto in "The Chemistry of the Hydrazo, Azo and Azoxy Groups", Part 1, ed. S.Patai, J.Wiley, London, 1975, p.462.
2. For example the 29 pages of the review cited in Ref.1 contain no reference to electrooxidation of azo or hydrazo compounds. However, see: T.M.Florence, F.J.Miller, and H.E.Zittel, Anal.Chem., 38, 1065 (1966); J.P.Stardins and V.T.Elezer in "Encyclopaedia of Electrochemistry of the Elements", ed. A.J.Bond, Decker, New York, 1978, XIII-4; M.Matrka, J.Marhold, and Z.Sagner, Coll.Czech.Chem.Comm., 34, 1615 (1969).
3. See for instance: J.Kelemen, Dyes and Pigments, 2, 73 (1981). The azo-hydrazo situation for 1-arylazo-2-naphthols is far from clear-cut, and we shall add further evidence on this problem in the future.
4. Controlled potential electrolyses were carried out in a 2-compartment electrolysis cell comprising a beaker and two platinum electrodes. The "second compartment" was a silver wire in a 0.1M Ag^+ solution in CH_3CN, acting as a reference electrode. The 3-compartment cell differed only in that the anode was separated from the bulk of the electrolyte solution by a glass sleeve fitted with a sinter disc. Transfer of solution from the anode compartment was thereby prevented, although current was unimpeded. Electrolyses were in purified CH_3CN containing 50% aqueous HBF_4 and $Et_4N^+BF_4^-$ (0.1M) as supporting electrolyte. The electrolyte was stirred throughout by a magnetic stirrer bar off-set from the centre of the beaker to improve mass transfer. Electrode potentials were typically 0.75-0.95V and current densities were 30-70mA/cm^2.
5. All new compounds have been characterised by elemental analysis, mass spectra, 100 or 360 MHz ^1H nmr, ^{13}C nmr, ir and uv/visible spectra. Solid phase ^{13}C nmr were obtained for some key products. Details of these measurements, as well as comparison with model compounds for (3) and (5), prepared by unambiguous alternative routes, will be reported in full papers.
6. Anilines are known to be electrooxidised to quinones: R.L.Hand and R.F.Nelson, J.Electrochem.Soc., 125, 1059 (1978).
7. Reduction was effected by refluxing an aqueous ethanol solution of (3) with sodium dithionite until the colour had faded to pale yellow.
8. Compound (8) (mp 97-98°C) was prepared in 98% yield from (1a) by CH_3I methylation in DMSO containing dimsyl anion as base. (Lit. mp 93-94°C: G.Charrier and G.Ferreri, Gazz.Chim. Ital., 42, 118 (1912).)

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