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Short Communications

Electrochemical Reduction of 4-Nitroisopropylbenzene in Sulfuric Acid

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Electrochemical reduction of aromatic nitro compounds in acid solution generally yields hydroxylamines which may be reduced to amines at a more negative potential or may undergo rearrangements.[1]

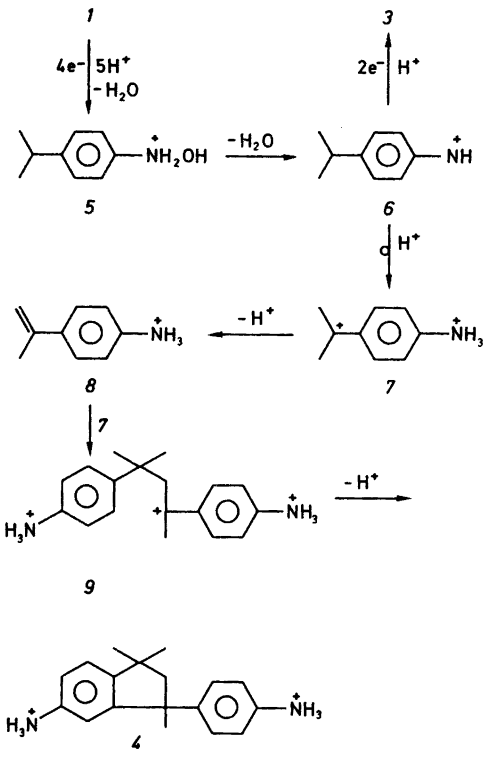
Aromatic nitro compounds bearing alkyl groups in suitable positions may thus give a number of products on reduction. Thus 5-nitroacenaphthene yields 5-aminoacenaphthene[2] in a 6-electron reduction which involves an elimination of water from the intermediate hydroxylamine akin to the reduction of *p*-nitrophenols; *p*-nitrotoluene is reduced to 2,5-dihydroxytoluene[3] in 25% sulfuric acid at 90 °C and to 4-amino-2'-methyl-5'-nitrodiphenylmethane in concentrated sulfuric acid.[4,5]

This communication describes another type of side-reaction during the reduction of an alkyl nitrobenzene, 4-nitroisopropylbenzene, (*1*) in sulfuric acid; the reduction leads to a derivative of styrene which reacts further by acid catalysis. It seems to be the first example of the introduction of a carbon-carbon double bond in an alkyl side-chain during the reduction of an aromatic nitro compound.

Results and discussion. A polarogram of *1* in concentrated sulfuric acid (*2*) showed a single wave with $E_{\frac{1}{2}} = -0.21$ V *vs.* Ag/AgCl.

Preparative reduction of *1* at a stirred mercury electrode in *2* yielded *p*-aminoisopropylbenzene (*3*) and 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindan (*4*) together with polymeric material, $n = 3.6$ F mol^{-1}. *4* has previously been obtained[6] from *p*-amino-α-methylstyrene (*8*) under acidic conditions.

On reduction of *1* in *2* at a platinum electrode *3*, *4*, and trace amounts of an unidentified substance were obtained. The formation of *3* and *4* may be explained by Scheme 1.



Scheme 1.

The electrode reaction is the expected 4-electron reduction of *1* to *p*-hydroxylaminoisopropylbenzene (*5*)which through *6* and *7* is transformed into *p*-amino-α-methylstyrene (*8*); *8*, which previously was prepared from *p*-nitro-α-methylstyrene, is dimerized to *4* in a known acid catalyzed reaction.

The formation of *4* through *8* thus illustrates one of the reaction routes available for *p*-alkylphenylhydroxylamines under acidic conditions; in sulfuric acid such reactions may be the main reactions and they may afford some of the side-products under less acidic conditions.

These reactions take place in strong sulfuric acid and some sulfonation of the amino derivatives

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probably occurs yielding water soluble products which have not been sought isolated; some material is also lost through polymerization of the intermediate styrene derivative.

Experimental. Apparatus. The cell has been described previously. A potentiostat from Juul electronics, Copenhagen, was used. For ^{1}H and ^{13}C NMR spectra a Varian CFT-20 and for mass spectra a Micromass 7070E were employed.

Materials. 4-Nitroisopropylbenzene (*1*) was obtained by nitration of isopropylbenzene according to Haworth and Barker.[7]

Electrolysis of 1 at a mercury cathode. 1 (5 g) was reduced in sulfuric acid; after the passage of about 4 F mol^{-1} the catholyte was slowly poured on ice. The aqueous solution was extracted with methylene chloride to remove unreacted *1* (0.4 g). The aqueous phase was made alkaline with concentrated ammonia and extracted four times with dichloromethane which was dried (K_2CO_3) and removed *in vacuo* leaving a residue, 2.58 g. The crude product was dissolved in 2 M HCl, sodium acetate added in slight excess, and the amines acetylated with acetic anhydride. The acetylated amines were extracted with chloroform, which was washed with water, dried and evaporated. The residue was separated on a column of silica using chloroform, 2 % methanol in chloroform, and 10 % methanol in chloroform as eluent. Isolated were 4-acetaminoisopropylbenzene (955 mg), m.p. 99 – 101 °C (102 °C)[7] and 5-acetamino-3-(4-acetaminophenyl)-1,1,3-trimethylindane (417 mg), m.p. 202 – 203 °C. ^{1}H NMR ($CDCl_3$): δ 1.05 (3 H, s), 1.29 (3 H, s), 1.57 (3 H, s), 2.04 (6 H, s), 2.12 (1 H, d, *J* 12 Hz), 2.32 (1 H, d, *J* 12 Hz) 6.85 – 7.60 (7 H, m), 8.63 (1 H, s), 8.70 (1 H, s). MS (*m/e*): 350 (M^+, 33), 335 (100), 293 (16). If the crude product was not acetylated *4* was isolated, albeit in lower yield, m.p. 94 – 97 °C (m.p. 93 – 94 °C).[6] ^{1}H NMR ($CDCl_3$): δ 1.02 (3 H, s), 1.26 (3 H, s), 1.58 (3 H, s), 2.12 (1 H, d, *J* 12.5 Hz), 2.30 (1 H, d, *J* 12.5 Hz), 3.5 (2 H, broad s), 6.35 – 7.15 (7 H, m). MS (*m/e*): 266 (M^+, 41), 251 (100), 236 (9), 221 (9), 158 (18).

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