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Synthesis of azo aromatic diacyl chlorides from nitro aromatic acids

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The synthesis of azo aromatic diacyl chlorides using glucose as the reductant of nitro aromatic acids is reported.

Keywords: nitro aromatic acid, azo aromatic diacyl chloride, glucose

It is well known that azo compounds are widely utilised as dyes[1] and analytical reagents[2] and in modern technology as materials for non-linear optics,[3] materials in optical information storage systems in laser disks and as oil-soluble dyes in photography.[4]

Azo chromophore functionalised polymers have been paid great attention to recently for their potential applications in the field of communications.[5-7] Azo polymers possess some interesting properties such as light-induced phase transition of liquid crystal polymers,[8] 'command surface', light-induced birefringence and dichroism.[9] Not surprisingly, polymers of this kind are increasingly viewed as attractive candidates for a variety of 'smart' materials applications. To develop new high performance materials endowed with stimuli-responsive properties, it is necessary to synthesise reactive azo aromatic diacyl chlorides.

In previous literature reagents including CAN,[10] NBS/pyridine,[11] $NaNO_2/NaHSO_4$. H_2O[12] and AMD/H_2SO_4/silica/gel[13] have been used as oxidants to synthesise azo compounds. Azo compounds can also be prepared by the standard (diazo-coupling) method.[14] These methods, however, cannot be used to synthesise azo aromatic diacyl chlorides.

Glucose is a well known reductant for the efficient and selective reduction of *p*-nitrobenzoic acid to azobenzene-4,4'-dicarboxylic acid.[15] We have now synthesised six azo aromatic diacids by a similar method. Azo aromatic diacyl chlorides were then obtained by reaction of the azo aromatic diacids with an excess of thionyl chloride. The structures of the products were confirmed by IR, ^1H NMR and elemental analysis (see the Scheme).

This method uses simple apparatus and the yields of the reaction are more than 75%. In conclusion, this is a convenient method for the preparation of azo aromatic diacyl chlorides from nitro aromatic acids.

Experimental

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a FTS-40 spectrophotometer in KBr. ^1H NMR spectra were measured on a Bruker DPX-400M spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on a PE-2400 CHN elemental analyser.

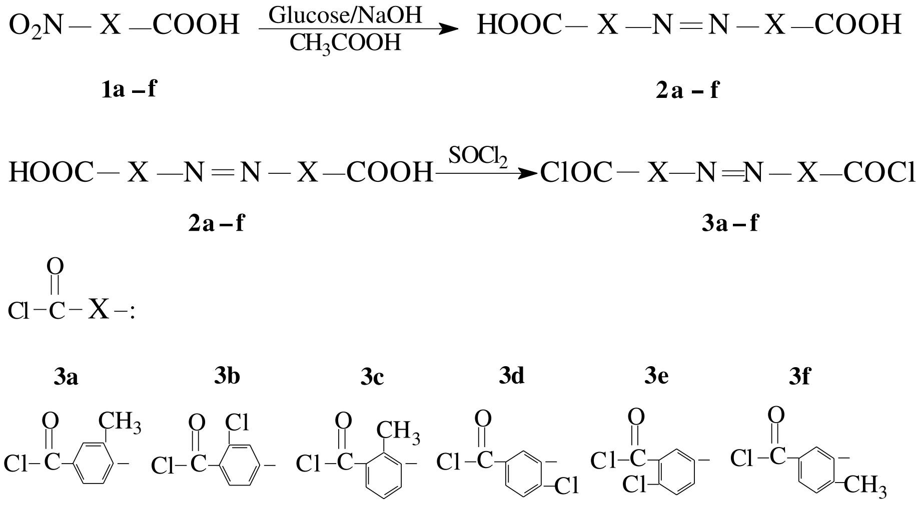
General procedure for the preparation of azo aromatic diacyl chloride **3a–f**

To a magnetically stirred solution of nitro aromatic acid (79 mmol) **1a–f**, NaOH (50 g, 1250 mml) and water (225 ml) at 60–65°C was added a warmed solution of glucose (100 g, 555 mmol) in water (150 ml) over 1 h. The reaction mixture was stirred vigorously in air for 8 h ultimately affording a viscous, dark brown mixture. On cooling to room temperature, the mixture was acidified with glacial acetic acid to pH 6, filtered, washed with water and dissolved in hot potassium carbonate solution. The solution was acidified, filtered and washed with water again. Crude azo aromatic diacids **2a–g** were obtained and used in the next step without purification.

The crude azo aromatic diacid (14.5 mmol) **2a–f**, 30 ml thionyl chloride and 0.2 ml triethylamine were placed in a 100 ml round-bottomed flask. The mixture was refluxed for 12 h, until the suspension mixture was converted into a clear solution. Unreacted thionyl chloride was removed under reduced pressure and the residue was recrystallised from *n*-heptane and dried below 80°C in a vacuum to yield the pure products. All the compounds gave satisfactory analytical and spectroscopic data.

The physical and spectroscopic data of compounds **3a–f:** *2,2'-dimethylazobenzene-4,4'-dicarboxylic acid chloride* **(3a):** Dark-brown needles; Yield 93 %; m.p. 181–183 °C; IR (KBr) ν: 3098, 2965, 2926, 1754, 1698, 1598, 1476, 1440 cm^{-1}; ^1H NMR δ: 2.82 (s, 6H, CH_3), 7.66 (d, 2H, ArH), 8.06(d, 2H, ArH), 8.15(s,2H,ArH); Anal. calcd. for $C_{16}H_{12}Cl_2N_2O_2$: C, 57.3; H, 3.6; N, 8.4. Found: C, 57.7; H, 3.7; N, 8.4.

3,3'-dichloroazobenzene-4,4'-dicarboxylic acid chloride **(3b):** Orange powder; Yield 88 %; m.p. 153–155 °C; IR (KBr) ν: 3095, 1766, 1701, 1586, 1561, 1464 cm^{-1}; ^1H NMR δ: 7.98 (d, 2H, ArH)



Scheme 1 Synthesis of azo aromatic diacyl chlorides.

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8.06 (s, 2H, ArH), 8.29 (d, 2H, ArH); Anal. calcd. for $C_{14}H_6Cl_4N_2O_2$: C, 44.7; H, 1.6; N, 7.45. Found: C, 45.1; H, 1.6; N, 7.7.

2,2'-dimethylazobenzene-3,3'-dicarboxylic acid chloride **(3c):** Orange needles; Yield 86 %; m.p. 185–186 °C; IR (KBr) ν: 3094, 2972, 2937, 1755, 1692, 1568, 1441 cm^{-1}; ^{1}H NMR δ: 2.95 (s, 6H, CH_3), 7.46 (t, 2H, ArH); 7.88 (d, 2H, ArH), 8.32 (d, 2H, ArH); Anal. calcd. for $C_{16}H_{12}Cl_2N_2O_2$: C, 57.3; H, 3.6; N, 8.4. Found: C, 57.7; H, 3.65; N, 8.4.

6,6'-dichlorioazobenzene-3,3'-dicarboxylic acid chloride **(3d):** Orange powder; Yield 78 %; m.p. 219–222 °C; IR (KBr) ν: 3085, 1758, 1690, 1583,1564,1465,1443 cm^{-1}; ^{1}H NMR δ: 7.78 (d, 2H, ArH), 8.19 (d, 2H, ArH), 8.47 (s, 2H, ArH); Anal. calcd. for $C_{14}H_6Cl_4N_2O_2$: C, 44.7; H, 1.6; N, 7.45. Found: C, 45.0; H, 1.65; N, 7.6

4,4'-chlorioazobenzene-3,3'-dicarboxylic acid chloride **(3e):** Orange powder; Yield 75 %; m.p. 177–179 °C; IR (KBr) ν: 3094, 1754, 1698, 1585, 1560, 1445 cm^{-1}; ^{1}H NMR δ: 7.70 (d, 2H, ArH), 8.13 (d, 2H, ArH), 8.69 (s, 2H, ArH); Anal. calcd. for $C_{14}H_6Cl_4N_2O_2$: C, 44.7; H, 1.6; N, 7.45. Found: C, 44.9; H, 1.7; N, 7.6

2,2'-dimethylazobenzene-5,5'-dicarboxylic acid chloride **(3f):** Orange powder; Yield 82 %; m.p. 170–172 °C; IR (KBr) ν: 3089, 2957, 2851, 1747, 1695,1595,1571, 1448 cm^{-1}; ^{1}H NMR δ: 2.86 (s, 6H, CH_3), 7.53(d, 2H, ArH), 8.15(d, 2H, ArH), 8.34(s, 2H, ArH); Anal. calcd. for $C_{16}H_{12}Cl_2N_2O_2$: C, 57.3; H, 3.6; N, 8.4. Found: C, 57.8; H, 3.7; N, 8.5.

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