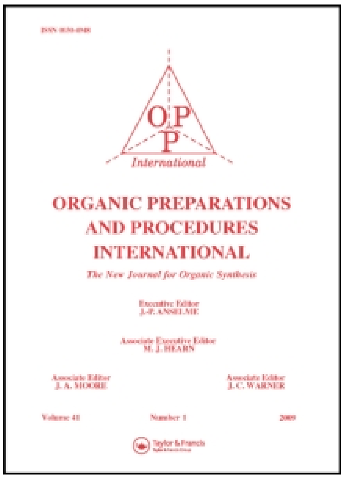

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TEMPERATURE DEPENDENT MIGRATION OF THE NITRO GROUP OF POTASSIUM 4-AMINO-3,5-DINITROBENZENESULFONATE VS DESULFONATION

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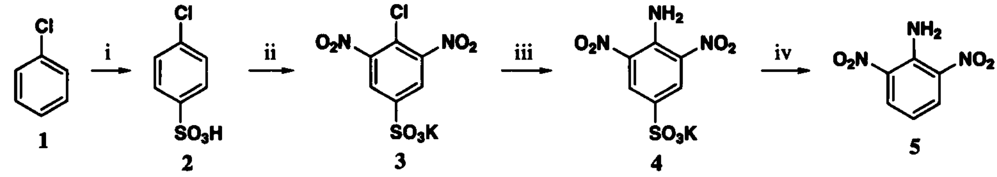
Electrophilic sulfonations of aromatic compounds such as naphthalene, performed under kinetic control, give products different from those carried out under thermodynamically controlled conditions.[1] The possibility of hydrolytic removal of the sulfonic acid group under relatively mild conditions makes it a suitable protecting group, a process which, for example, has been claimed for the preparation of 2,6-dinitroaniline (**5**), starting from chlorobenzene (*Scheme 1*).[2] However, using this procedure[2] we obtained a mixture of 2,6- and 2,4-dinitroanilines from potassium 4-amino-3,5-dinitrobenzenesulfonate (**4**) which contains up to 20% of the second isomer (estimated by integrated intensity from ^{1}H NMR) which is practically impossible to separate from the desired product; 2,4-dinitroaniline has been obtained cleanly by ammonolysis of 2,4-dinitrochlorobenzene.



i) H_2SO_4-SO_3, 100°C; ii) addition of KNO_3, 40-60°C (i, ii one pot); iii) NH_3-H_2O, reflux; iv) H_2SO_4-H_2O, reflux

Nitrative desulfonation of aromatic compounds is a known procedure for the introduction of the nitro group; for example, it has been exploited for the manufacture of TNT from toluene-2,4,6-trisulfonic acid whereby the sulfonic groups are replaced by nitro groups from nitric acid used in excess. *Ipso*-nitrations have been described by Fischer and Henderson.[3] On the other hand, the migration of the nitro group on aromatic skeletons is not common; in these cases, only one nitro group migrates from *position 2*, thus constituting 1,3-rearrangements of 2,3-dinitroacetanilide (to 2,5-dinitroacetanilide), 2,3-dinitroaniline and 2,3-dinitrophenol (to 2,5-dinitroaniline and 2,5-dinitrophenol)[4] or 2,3-dinitro-4-methylaniline (to 3,5-dinitro-4-methylaniline).[5] Although other examples of the migration of nitro group have been reported,[4] aromatic nitration is generally considered to be irreversible.

The reaction tandem shown in *Scheme 1,* carried out on the reported scale and scaled up six times, led us to conclude that during the nitration with potassium nitrate, 4-chloro-3-nitrobenzenesulfonate or 4-chloro-3,5-dinitrobenzenesulfonate (**3**) were generated in the first step; they were first desulfonated and then immediately nitrated at the position *para* to the chlorine atom (perhaps involving also *ipso*-nitration); this is probably due to the temperature of the reaction since the reaction mixture was heated to about 110-115°C for 20 hours after the addition of the whole amount of potassium nitrate (not completely dissolved). Another route to the 2,4-dinitroaniline isomer is *via* the incomplete sulfonation of the chlorobenzene.[6] Thermal isomerization of 2,6-dinitroaniline in sulfuric acid was not detected under similar conditions, even upon prolonged reaction times.

Two equal batches of potassium 4-amino-3,5-dinitrobenzenesulfonate (**4**) were subsequently desulfonated using the same concentration and amount of sulfuric acid. The first batch underwent desulfonation under strict temperature control, affording a mixture of isomers. The second batch was desulfonated by plunging the flask in a silicone oil bath pre-heated to 190-200°C which started a very vigorous reflux and produced pure 2,6-dinitroaniline (**5**) as the sole product.

Since there was no nitric acid, potassium nitrate or other source of nitronium ion in the reaction medium, the nitro group at *position 4* could only have come from migration of the nitro group *ortho* to the amino group before or after desulfonation. Desulfonation (step iv, *Scheme 1*) of the 4-amino-3,5-dinitrobenzenesulfonate can be performed using the same concentration of sulfuric acid, but the reflux must be as vigorous as possible. Consequently, we recommend the use of an intense heat source, such as a heating mantle, microwave or a magnetic stirrer with powerful heater, in order to avoid production of the mixture of isomers.

EXPERIMENTAL SECTION

Commercial reagents (chlorobenzene, sulfuric acid (96%), potassium nitrate, ammonia water (26%) were used without further purification, drying or other modification. Melting points were measured using a Boetius apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Tesla BS 487 (80 MHz) and a Varian VXR-300 spectrometers referenced to the external TMS in $CDCl_3$. 4-Amino-3,5-dinitrobenzenesulfonate was prepared as its potassium salt according to reported procedure (*Scheme,* i – iii*)*.[2]

Preparation of 2,6-Dinitroaniline (5).- A suspension of the damp potassium 4-amino-3,5-dinitrobenzenesulfonate (obtained from a normal batch scale as described in *ref.* 2) in water (200 mL) and sulfuric acid (200 mL, 96%) in a flat bottom 1000 mL flask was heated and stirred with a high torque magnetic stirrer (920 W Schott) and a robust magnetic stirring bar. After addition of the acid, the reaction mixture was immediately heated to vigorous boil (up to 200°C) for 6 hrs (vigorous reflux is required in order to avoid the formation of 2,4-dinitroaniline). After cooling the reaction mixture overnight at 15°C, 2,6-dinitroaniline (30-36 g, 33-40% yield from **1**) was obtained as gold-colored plates which were washed with water to remove most of the sulfuric acid and recrystallized from ethanol using charcoal. Similar results were obtained when the collected solid was dissolved in dichloromethane (40-60 mL), followed by addition of water (100 mL) and neutralization with aqueous ammonia or sodium bicarbonate; separation of the dichloromethane layer followed by treatment with charcoal, filtration and evaporation *in vacuo* gave 28-34 g (31-38%) of **5** as a yellow solid, mp. 138-142°C; *lit.*[2] 139-140°C.

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