Isolation and Further Reactions of Charged Species resulting from *ipso*-attack in the Nitration of Aromatic Amines

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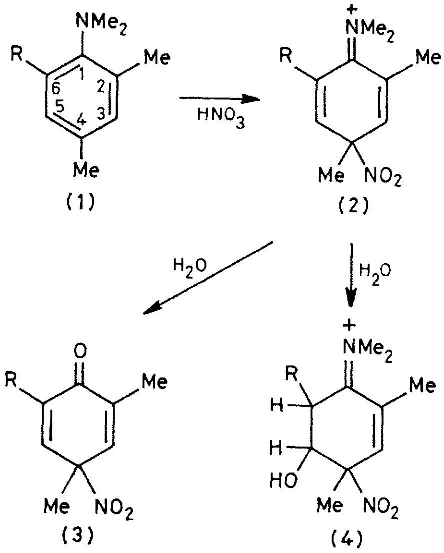
Summary Charged species resulting from *ipso*-attack in the nitration of aromatic amines can be precipitated as hexafluorophosphates but the isolation is complicated by addition and substitution reactions involving water in the solvent.

PREVIOUS work has established[1] that the nitration of *NN*-dimethyl-*p*-toluidine in aqueous sulphuric acid proceeds in two clearly separated stages: the formation of a σ-complex by *ipso*-attack at the 4-position and the rearrangement of this ion to give the 2-nitro product. The work now reported concerns an extension of these studies to related amines (**1**; R = H, Me, or NO_2).

When the intermediate σ-complex has at least one unsubstituted position *ortho* to the dimethylamino group [*e.g.* (**2**; R = H)], the rearrangement of the nitro-group to this position normally takes precedence over other reactions. When both of these *ortho*-positions are blocked, the reaction, under some conditions, stops at the σ-complex stage. Thus, the reaction of the amine (**1**; R = Me) at 0 °C with aqueous nitric acid (70%) gives the ion (**2**; R = Me) and this can be precipitated as the hexafluorophosphate by pouring the reaction mixture into a saturated solution of potassium hexafluorophosphate. In more aqueous nitric acid (40%), the formation of the ion (**2**; R = Me) is rapidly followed by nucleophilic attack by the solvent at C-1 and the cyclohexadienone (**3**; R = Me) is precipitated as an oil in a yield of 75%. This reaction is analogous to the replacement of –OMe by –OH following *ipso*-attack at the 4-methyl group in the nitration of aromatic ethers.[2]

The reaction of the amine (**1**; R = NO_2) with aqueous nitric acid (70%) at 0 °C takes a different course for the ^1H n.m.r. spectrum of the intermediate σ-complex (**2**; R = NO_2) is not observed in the solution. This appears to be because the σ-complex reacts rapidly with water, for the adduct (**4**; R = NO_2) is formed and can be precipitated as the hexafluorophosphate by the method outlined above. Conjugative electron withdrawal by the nitro-group at the 6-position should favour nucleophilic attack at the 5-position rather than the 1-position and can hence explain this change in the position of reaction with the solvent.



The evidence for the structures of the above compounds is based on ^1H and ^{13}C n.m.r. spectra but the two hexafluorophosphate salts also give good elemental analyses and the cyclohexadienone (**3**; R = Me) was shown to be identical with a sample prepared by the nitration of the corresponding phenol.[3] The differences ($\Delta\delta$) between the ^{13}C chemical shifts of the adduct (**4**; R = NO_2) and the corresponding amine (Table) show clearly the upfield shifts of the lines for the three carbon atoms that change from sp^2 to sp^3 hybridisation in forming the adduct.

TABLE. ^{13}C Chemical shifts[a] of the ring carbon atoms for the amine (**1**; R = NO_2) and the adduct (**4**; R = NO_2).

	(**1**; R=NO_2)[b]	(**4**; R=NO_2)[c]	$\Delta\delta$ ^{13}C
C-1	148·1	170·8	22·7
C-2	133·7	137·5	3·8
C-3	135·4	143·1	7·7
C-4	138·7	89·9	−48·8
C-5	122·4	74·7	−47·7
C-6	142·1	89·1	−53·0

[a] In p.p.m. from Me_4Si; downfield shifts positive. [b] In $CDCl_3$ at 25 °C. [c] In 70% nitric acid at 0 °C.

The mechanism of the above reactions is being investigated: it is already clear that the formation of all three intermediates (**2**; R = H, Me, or NO_2) requires the presence of nitrous acid in the medium.

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