Nitration of *NN*-Dimethyl-*p*-toluidine. Spectroscopic Evidence for the Bulk Formation of a σ-Complex Formed by *ipso*-Attack

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Summary In 70—77% sulphuric acid, the nitration of *NN*-dimethyl-*p*-toluidine proceeds in two clearly separated stages: the formation of the σ-complex (I) by *ipso*-attack and the slow rearrangement of this ion to the nitro-compound (II).

Many nitrations are now recognised to occur through rearrangement of σ-complexes formed by *ipso*-attack.[1] Evidence for these intermediates comes partly from the addition products formed by reaction of the σ-complexes with nucleophiles and partly from the rationalisation of variations in the product composition in terms of competing reactions available to the σ-complexes. However, except for fully substituted aromatic compounds (*e.g.* hexamethylbenzene),[2] the σ-complexes resulting from *ipso*-attack have not been directly observed under the conditions used for nitration.

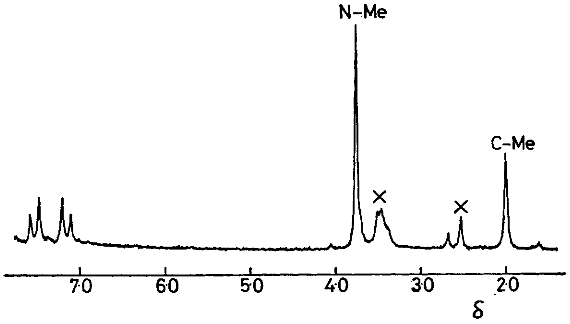
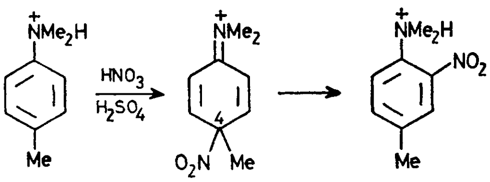


Figure. The 100 MHz ^1H n.m.r. spectrum of the intermediate (I) at 0 °C in 77·4% sulphuric acid started 39 min after mixing the reagents (0·5 mol dm^{-3}). The peaks marked × derive from the small amount of product (II) present.



(I) (II)

We now have evidence that the NMe_2 group is capable of stabilising one such intermediate so that the corresponding nitration may occur in two clearly separated stages. The overall reaction of *NN*-dimethyl-*p*-toluidine with nitric acid in 70—77% sulphuric acid at 0 °C gives the mono-nitro-compound (II) (isolated yield 78%). The conjugate acids of both this product and the initial amine show the expected doublet in the ^1H n.m.r. spectrum of the *N*-methyl protons because of coupling with the hydrogen on the nitrogen. In the corresponding spectrum of the intermediate, the peak of the *N*-methyl protons is shifted to low field and appears as a singlet while that of the *C*-methyl protons is shifted to high field. These features and the spectrum of the aromatic protons (see Figure) are consistent with the σ-complex (I).

This identification is confirmed by the differences between the ^{13}C n.m.r. spectra of the intermediate and the initial amine (see Table) and particularly by the marked upfield shift ($\Delta\delta$ ^{13}C −34·0 p.p.m.) attributed to the change in hybridisation at C-4. This chemical shift is very similar to that for the corresponding carbon atom in the formation of the σ-complex from hexamethylbenzene and the nitronium ion (−33·6 p.p.m.).[2]

Table

^{13}C Chemical shifts[a] for *NN*-dimethyl-*p*-toluidine (III) and the σ-complex (I).

Sub-strate	C-1	C-2 and -6	C-3 and -5	C-4	Me–C	Me–N
(III)[b]	148·5	112·6	129·2	124·6	19·8	40·1
(I)[c]	166·1	125·5	153·3	90·6	29·9	49·8
$\Delta\delta^{13}C$	17·6	12·9	24·1	−34	10·1	9·7

[a] In p.p.m. from Me_4Si; downfield shifts positive. [b] In C_2D_6SO at 25 °C. [c] In 74·5% sulphuric acid at −10 °C.

The formation of the intermediate (I) is catalysed by nitrous acid, probably by the mechanism reported previously.[3]† The rearrangement of the intermediate to the product (II) obeys approximate first-order kinetics (k_1 = 7·4 × 10^{-4} s^{-1} for reaction at 0 °C in 74·5% sulphuric acid) and the first-order rate coefficient decreases with increasing acidity.

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† We do not believe that this catalysis occurs through 4-nitrosation followed by oxidation for, at these acidities, the reaction between nitrous acid and the amine is much slower and leads to demethylation at the nitrogen, (see ref. 4).

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[3] J. C. Giffney, D. J. Mills, and J. H. Ridd, *J.C.S. Chem. Comm.*, 1976, 19.

[4] D. J. Mills, Ph.D. thesis, London, 1976.