ipso-Attack in the Nitration of Aromatic Amines. Part 2.[1] Isolation of Salts and Other Products resulting from *ipso*-Attack

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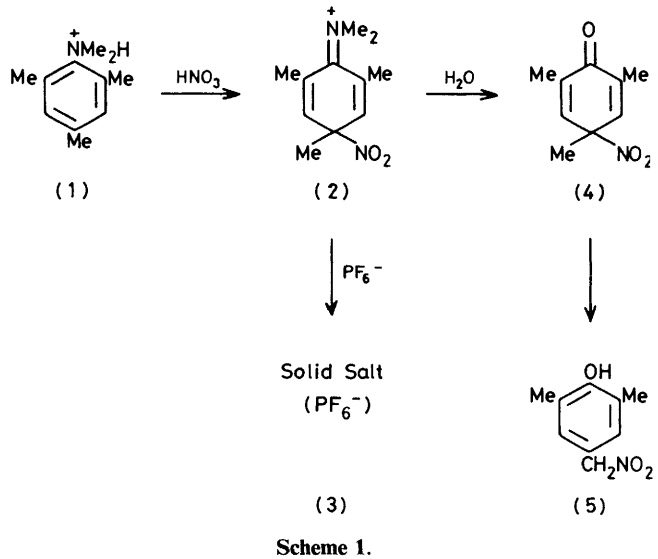
In 70% nitric acid at 0 °C, *NN*,2,4,6-pentamethylaniline undergoes *ipso*-attack at the 4-position to form the relatively stable *ipso*-intermediate (2); this ion can be precipitated as the hexafluorophosphate. In more aqueous media, the dimethylamino group is displaced by water to form the hexadienone (4). In aqueous nitric acid at 0 °C, *NN*,2,4-tetramethyl-6-nitroaniline undergoes both *ipso*-attack and addition of water to the ring to form the adduct (8); this ion can also be precipitated as the hexafluorophosphate. The reaction of *NN*,2,6-tetramethyl-4-methoxyaniline with 52% nitric acid at 0 °C also involves displacement of the dimethylamino group and gives finally 2,6-dimethylbenzoquinone. The initial stages of the reactions of the above amines require the presence of nitrous acid and the reactions are inhibited by hydrazine.

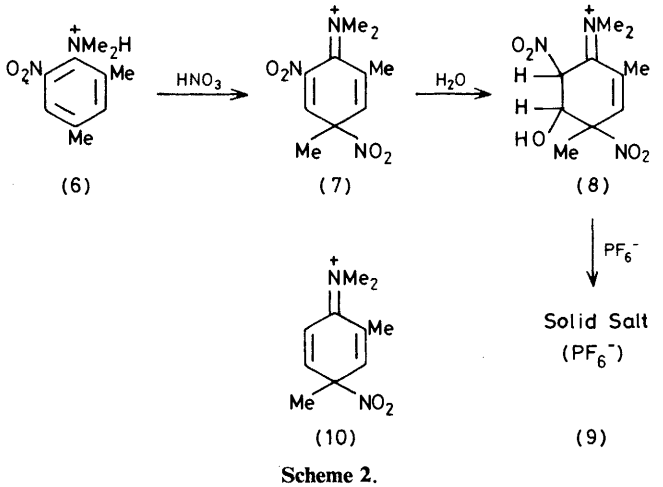
The work described in Part 1 of this series [1] provided evidence for *ipso*-attack in the nitration of some *para*-substituted aromatic amines and for the 1,3-rearrangement of the nitro group in the intermediates formed by *ipso*-attack. Our subsequent work has shown that this rearrangement is one of a number of possible reaction paths following *ipso*-attack.[2] The present paper is concerned with some of the other reaction paths and also with the isolation of salts of the ionic intermediates formed by *ipso*-attack.

NN,2,4,6-*Pentamethylaniline*.—The reaction of the conjugate acid (1) of this amine with nitric acid in aqueous sulphuric acid to form the *ipso*-intermediate (2) (Scheme 1) was reported in Part 1.[1] The reaction has now been investigated using nitric acid at various concentrations as the solvent. In 70% nitric acid containing a trace of nitrous acid, the formation of the *ipso*-intermediate occurs smoothly at 0 °C and this ion can be precipitated as the hexafluorophosphate (3). The resulting white crystals are stable at −25 °C but decompose at room temperature giving off brown fumes. When the white crystals are re-dissolved in 70% nitric acid, the ^{13}C n.m.r. spectrum shows the presence of the intermediate (2) (Table 1). The assignment of the lines in the ^{13}C spectrum of the ion (2) was discussed in Part 1; [1] this assignment is supported by the ^{13}C n.m.r. spectrum of the ^{15}N doubly labelled ion and the corresponding coupling constants (J_{NC}) are included in Table 1.

When the same reactions are carried out in 40% nitric acid at 0 °C, the formation of the ion (2) is followed by the slow displacement of the dimethylamino group and the dienone (4) separates as an oil. The identity of this product was established by a comparison of the u.v. spectrum and the ^1H and ^{13}C n.m.r. spectra of the oil with those of a sample of the dienone prepared by the oxidation of 2,4,6-trimethylphenol with fuming nitric acid.[3] The displacement of the dimethylamino group in 40% nitric acid is easily observed from the appearance in the ^1H n.m.r. spectrum of the characteristic triplet of the dimethylammonium ion (δ 2.82). The dienone (4) as the oil, or as a solution in chloroform, slowly rearranges to give the phenol (5): this reaction has been observed previously.[4] Details of the ^{13}C n.m.r. spectra of products (4) and (5) are included in Table 1.



Scheme 1.



Scheme 2.

NN,2,4-*Tetramethyl*-6-*nitroaniline*.—The replacement of one of the *ortho*-methyl groups of the anilinium ion (1) by a nitro group causes a marked change in the type of product formed in aqueous nitric acid. The ion (6) (Scheme 2) reacts in 52% and 70% nitric acid at 0 °C in a process that is catalysed by nitrous acid and inhibited by hydrazine (a nitrous acid scavenger). By analogy with the reactions of other amines, this process should lead to the *ipso*-intermediate (7), and some transitory peaks that may derive from the ^1H n.m.r. spectrum of this intermediate are seen. However, the spectrum indicates

Table 1. ^{13}C Chemical shifts (p.p.m. from Me_4Si) for the compounds listed in Scheme 1; the values in parentheses are J_{NC}/Hz in the ^{15}N doubly labelled *ipso*-intermediate

Substrate	C-1	C-2, -6	C-3, -5	C-4	Me-4	Me-2, -6	Me-N
(2) [a]	175.1	137.1	141.4	87.7	23.3	19.2	48.8
(2) [b]	175.9	137.6	142.5	87.7	24.4	20.5	49.7
	(20.5)			(5.6)			(7.0)
(3) [c]	175.6	137.4	141.5	87.4	23.3	19.3	48.9
(4) [d]	185.1	137.3	138.2	84.9	26.2	15.9	
(5) [d]	153.8	121.6	130.5	123.9	79.9	15.8	

[a] In 70% HNO_3 at 0 °C. [b] In 72.3% H_2SO_4 at 0 °C (ref. 1). [c] As (*a*) but re-dissolved after isolation. [d] In $CDCl_3$.

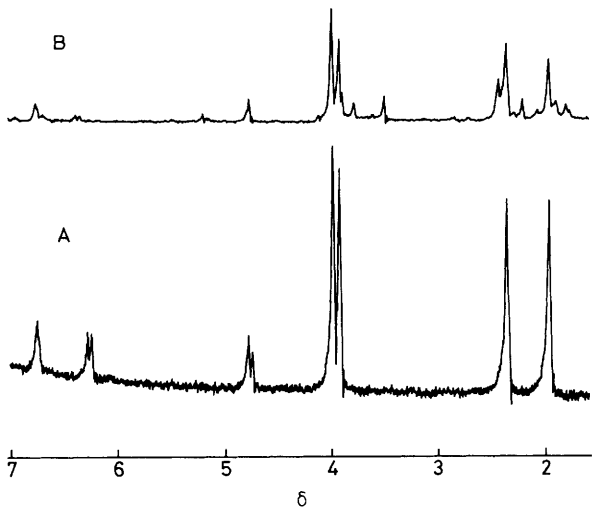
Table 2. ^{13}C Chemical shifts (p.p.m. from Me_4Si) at 0 °C for the compounds in Scheme 2

Substrate	C-1	C-2	C-3	C-4	C-5	C-6	Me-2	Me-4	Me-N	
(6) [a]	148.1	133.7	135.4	138.7	122.4	142.1	20.4	18.2	42.1	
(9) [b]	170.8	137.5	143.1	89.9	74.7	89.1	20.7	19.2	46.8	49.0
Δδ	22.7	3.8	7.7	−48.8	−47.7	−53.0	0.3	1.0	4.7	6.9

[a] As the free amine in $CDCl_3$. [b] In 70% nitric acid.

Table 3. ^1H Chemical shifts (δ values) in 70% nitric acid at 0 °C for the compounds in Scheme 2

Substrate	H-3	H-5	H-6	Me-2	Me-4	Me-N	
(6)	7.67	8.11		2.73	2.39	3.62 (d)	
(9)	6.77	4.78 (d)	6.28 (d)	2.36	1.98	3.98	3.92
Δδ	−0.90	−3.33		−0.37	−0.41	0.36	0.30



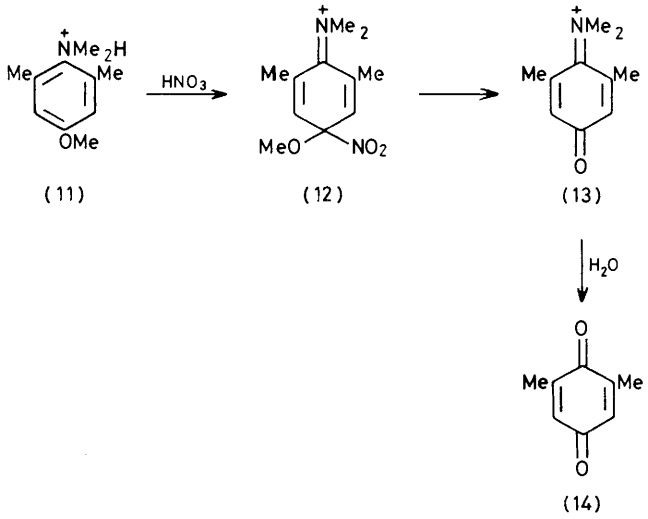
The ^1H n.m.r. spectra of (A) a solution of the salt (9) in 70% nitric acid at 0 °C, and (B) the reaction mixture for the formation of this salt from *NN*,2,4-tetramethylaniline in 52% nitric acid at 0 °C in a medium containing 76% deuterium

that further reaction occurs to give a major product that can be precipitated as the hexafluorophosphate salt (9). The stoicheiometric composition of this salt shows that it corresponds to the hexafluorophosphate of the expected *ipso*-intermediate plus one water molecule. The salt is stable at −25 °C but decomposes at room temperature.

The ^{13}C n.m.r. spectrum of this salt when re-dissolved in 70% nitric acid at 0 °C is analysed in terms of structure (8) and compared with that of the corresponding free amine in Table 2. The high field shift of *ca.* 50 p.p.m. shown by the peaks of three of the carbon atoms accords with the change from sp^2 to sp^3 hybridisation and hence with the addition of a water molecule to one of the double bonds in the *ipso*-intermediate. The ^1H n.m.r. spectrum of the salt under the same conditions is shown in the Figure (A) and analysed in Table 3. The assignment of the peaks is helped by comparison with the spectrum obtained following the preparation of the adduct in a partly deuteriated solvent [Figure (B)]. The much reduced intensity of the peak at δ 6.28 shows that this peak comes from the added water molecule. The other peaks in the Figure (B) arise from minor products of the reaction: these remain in solution when the major product is precipitated as the hexafluorophosphate. The structure of the adduct (8) implies that a number of stereoisomers could be present but the relatively simple form of the ^1H n.m.r. spectrum [Figure (A)] suggests that one of these predominates: the information from the spectrum is insufficient for this to be identified.

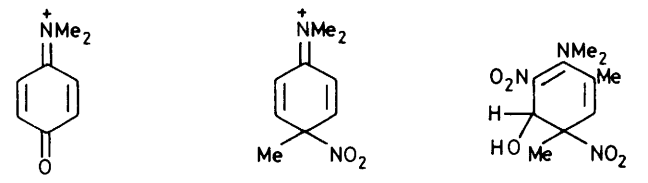
The adduct (8) can also be prepared by dissolving *NN*,2,4-tetramethylaniline in 52 or 70% nitric acid. When 70% nitric acid is used, the conversion into the corresponding *ipso*-intermediate (10) can be seen in the ^1H n.m.r. spectrum, followed by the 1,3-rearrangement to yield the nitro-product (6): this then reacts further as described above. When 52% nitric acid is used, the peaks of the *ipso*-intermediate (10) are not seen, presumably because the rate of the 1,3-rearrangement increases with a decrease in the acidity.[1] The reaction of *NN*,2,4-tetramethylaniline in 70% nitric acid can be made to yield the nitro-product (6) by adding hydrazine to the solution when the n.m.r. spectrum indicates that the formation of the *ipso*-intermediate (10) is complete: this does not hinder the 1,3-rearrangement of the nitro group in the intermediate (10) but inhibits subsequent *ipso*-attack. The nitro-product (6) appears to be a new compound.

NN,2,6-*Tetramethyl*-4-*methoxyaniline*.—The reactions of this amine in 52% nitric acid have been studied at 0 °C. In the



(11) (12) (13) (14)

Scheme 3.



(15) (16) (17)

presence of hydrazine, no reaction occurs; the ^{1}H n.m.r. spectrum under these conditions is given in Table 4. The N–Me peak is a doublet because of coupling with the proton (J 5 Hz), and two CMe peaks are seen because of the conformation of the $\overset{+}{N}HMe_2$ group. This splitting of the CMe absorption is found also in the spectrum of the pentamethylanilinium ion (1). In the absence of hydrazine, reaction is rapid and none of the starting material is seen in a ^{1}H n.m.r. spectrum taken immediately after the addition of the amine to the acid. By analogy with the reactions of other amines, the first-formed species should be the *ipso*-intermediate (12), and the observed spectrum is in accord with this (Table 4) since the *N*-methyl peak is shifted to low field and the H-3,5 peak to high field. However, in some related studies of the reactions of *N*,*N*-dimethyl-4-methoxyaniline with nitric acid in aqueous sulphuric acid,[5] the first stable intermediate appeared from the ^{13}C n.m.r. spectrum to be the ion (15), and hence the intermediate in the present reaction could be either (12) or (13). In 52% nitric acid at 0 °C, this intermediate reacts further in a moderately slow reaction leading to the displacement of the NMe_2 group and to the appearance of the characteristic triplet of the $\overset{+}{N}Me_2H_2$ ion in the ^{1}H n.m.r. spectrum. Most of the reaction is complete after about 15 min and extraction of the reaction mixture then gives 2,6-dimethylbenzoquinone (14).

Discussion

The discussion in Part 1 [1] was mainly concerned with the 1,3-rearrangement of nitro groups in *ipso*-intermediates possessing unsubstituted *ortho*-positions: such rearrangements can then lead to proton loss from the Wheland intermediate and the formation of a normal nitro-product. In the compounds considered in this paper, the positions *ortho* to the amino group are occupied by other substituents. The type of 1,3-rearrangement considered previously cannot then lead to substitution unless a group is displaced and other reactions of the *ipso*-intermediates become more important. At the acidities used in the present work, the most significant of these reactions involves attack by water in the solvent.

Table 4. ^{1}H Chemical shifts (δ values) in 52% nitric acid at 0 °C for the compounds in Scheme 3

Substrate	H-3, -5	Me-2, -6	Me–N	Me–O
(11)	6.76	2.42, 2.52	3.42 (d)	3.78
(12) or (13)	6.57	2.44	3.89	3.80
(14)	6.65	1.98		

A number of the characteristics of the reactions with water are as expected. The rate of the reaction should increase with a decrease in the acidity of the medium because of the consequent increase in the activity of water. In 73.5% sulphuric acid or 70% nitric acid, the *ipso*-intermediate (2) is stable for many hours at 0 °C but, in 40% nitric acid at this temperature, the displacement of the dimethylamino group by water is almost complete in 3 h (Scheme 1). This reaction may be helped by the steric interactions in the initial state since the 1,3-rearrangement of the nitro group in the *ipso*-intermediate (16) has been studied in 25% sulphuric acid without complications from the displacement of the dimethylamino group by water.[2b] The rate of attack by water on the *ipso*-intermediate should be increased by electron-withdrawing substituents. It is interesting therefore that the attack of water on the *ipso*-intermediate (7) is so fast that the n.m.r. peaks of the intermediate can barely be detected even in 70% nitric acid at 0 °C (Scheme 2).

The attack of water at the 1-position of the ion (2) (Scheme 1) is analogous to the displacement of the methoxy group by water following *ipso*-attack at the *para*-position in the nitration of *para*-methylanisole.[6] The addition of a water molecule to a C=C double bond as shown in Scheme 2 has not, as far as we know, been observed to follow other examples of *ipso*-nitration. The difference in the position of attack of water on ions (2) and (7) can be rationalised by noting that while the $=\overset{+}{N}Me_2$ group activates the 1-, 3-, and 5-positions to nucleophilic attack, the activation by the nitro group in ion (7) is mainly limited to the 5-position (because of the positions of the double bonds in the ion). The attack of a water molecule at the 5-position followed by proton loss would give the enamine (17) and, since enamines undergo protonation on carbon,[7] the final product should be the adduct (8) as observed.

The *para*-methoxy-substituted ion (11) could in principle undergo *ipso*-attack at both C-1 and C-4, but the low field shift of the NMe proton signal in the ^{1}H n.m.r. spectrum of the intermediate (Table 4) points strongly to the formation of the normal *ipso*-intermediate (12) [or the related ion (13)]. Reactions involving *ipso*-attack at a methoxy group have been observed previously in the reaction of 1,2,3,5-tetramethoxybenzene with nitric acid in acetic anhydride.[8] It is interesting that the final product observed then was 2,6-dimethoxybenzoquinone; that series of reactions is analogous to the formation of 2,6-dimethylbenzoquinone in the present work (Scheme 3). Thus much of the present work extends to the nitration of amines the type of reactions already recognised to follow *ipso*-attack in the nitration of aromatic ethers. The special features of the amine reactions are the nitrous acid catalysis of *ipso*-attack,* the isolation of ionic intermediates

* *ipso*-Attack without nitrous acid catalysis has been observed in the nitration of some other anilinium ions.[9]

as the hexafluorophosphate salts, and the addition of water to a carbon double bond in one of the *ipso*-intermediates.

Experimental

Materials.—2,4-Dimethylaniline, 2,6-dimethylaniline, and 2,4,6-trimethylaniline were commercial samples. *N*-Methylation was carried out using trimethyl phosphate [10] giving *NN*,2,4-tetramethylaniline, δ($CDCl_3$) 2.26 (6 H, d), 2.65 (6 H, s), and 6.93 (3 H, s), b.p. 101—103 °C at 22 mmHg (lit.,[11] 203 °C at 760 mmHg) (Found: C, 80.3; H, 10.0; N, 9.5. Calc. for $C_{10}H_{15}N$: C, 80.5; H, 10.1; N, 9.4%); *NN*,2,6-tetramethylaniline, δ($CDCl_3$) 2.26 (6 H, s), 2.8 (6 H, s), and 6.96 (3 H, s), b.p. 89—91 °C at 17 mmHg (lit.,[12] 195—196.2 °C at 749 mmHg) (Found: C, 80.5; H, 10.2; N, 9.5%); *NN*,2,4,6-pentamethylaniline, δ($CDCl_3$) 2.25 (9 H, s), 2.8 (6 H, s), and 6.81 (2 H, s), b.p. 107—109 °C at 20 mmHg (lit.,[13] 93.5—94 °C at 12 mmHg) (Found: C, 80.7; H, 10.3; N, 8.7. Calc. for $C_{11}H_{17}N$: C, 80.9; H, 10.5; N, 8.6%).

NN,2,4-*Tetramethyl*-6-*nitroaniline* was prepared by the nitration of *NN*,2,4-tetramethylaniline (10 g) in nitric acid (70%; 100 cm^3) at 0 °C. Sodium nitrite (0.2 g) was added to catalyse the formation of the *ipso*-intermediate, followed after a few minutes by an excess of hydrazine to stop subsequent reactions. The mixture was then stirred for 2 h, quenched with water (1 dm^3), and extracted with methylene chloride. The product, after purification by t.l.c. [light petroleum (b.p. 40—60 °C)–methylene chloride–ethyl acetate (6 : 4 : 1) as eluant] had b.p. 149—151 °C at 14 mmHg, δ($CDCl_3$) 2.26 (6 H, s), 2.7 (6 H, s), and 7.13 (2 H, s) (Found: C, 62.0; H, 7.2; N, 14.6. $C_{10}H_{14}N_2O_2$ requires C, 61.8; H, 7.3; N, 14.4%); yield, 76%.

The preparation of *NN*,2,6-tetramethyl-4-methoxyaniline involved a series of reactions starting with the nitrous acid catalysed nitration of *NN*,2,6-tetramethylaniline in 70% nitric acid in a similar way to that described above.[2b] Demethylation at nitrogen occurs during the reaction giving N,2,6-*trimethyl*-4-*nitroaniline*, m.p. 100—101 °C, δ($CDCl_3$) 2.23 (6 H, s), 3.06 (3 H, s), 3.8 (1 H, s), and 7.83 (2 H, s) (Found: C, 59.8; H, 6.8; N, 15.7. $C_9H_{12}N_2O_2$ requires C, 60.0; H, 6.7; N, 15.6%). This was methylated by heating with a two-fold excess of dimethyl sulphate at 100 °C for 5 h. The excess of dimethyl sulphate was hydrolysed with aqueous sodium hydroxide and the resulting *NN*,2,6-tetramethyl-4-nitroaniline separated by filtration and purified by t.l.c. as described above; m.p. 66 °C (lit.,[14] 67—68 °C). This nitrocompound was reduced (Sn–HCl) to the corresponding amine, which was diazotised and the diazonium ion heated under reflux with methanol. The products, *NN*,2,6-tetramethylaniline and *NN*,2,6-tetramethyl-4-methoxyaniline, were separated by column chromatography using first light petroleum spirit (b.p. 40—60 °C)–methylene chloride (4 : 1) and then a more polar eluant with increasing amounts of ethyl acetate. The NN,2,6-*tetramethyl*-4-*methoxyaniline* was recovered as a yellow oil, δ($CDCl_3$) 2.26 (6 H, s), 2.8 (6 H, s), 3.73 (3 H, s), and 6.53 (2 H, s) (Found: C, 74.0; H, 9.6; N, 7.9. $C_{11}H_{17}NO$ requires: C, 73.7; H, 9.6; N, 7.8%).

The ^{15}N-labelled *NN*,2,4,6-pentamethylaniline was prepared by the nitration of mesitylene with $H^{15}NO_3$ in acetic anhydride–acetic acid [15] followed by reduction (Sn–HCl) to the amine and methylation with trimethyl phosphate.[10] The product gave satisfactory ^1H and ^{13}C n.m.r. spectra. The $H^{15}NO_3$ used (95—99% ^{15}N) was supplied by Prochem as an aqueous solution (43.5% $H^{15}NO_3$). *NNN*-Trimethylanilinium hexafluorophosphate used as an n.m.r. standard was prepared by Dr. P. F. Christy (Found: C, 38.5; H. 4.9; N, 4.9. Calc. for $C_9H_{14}F_6NP$: C, 38.4; H, 5.0; N, 5.0%). The nitric acid and sodium nitrite used were AnalaR reagents. Hydrazine was added to reaction mixtures as hydrazine sulphate (laboratory reagent).

N.m.r. Measurements.—A Varian T60 spectrometer was used for the ^1H n.m.r. measurements on compounds in $CDCl_3$, and a Varian HA100 spectrometer for the corresponding measurements on reaction products in aqueous nitric acid. The NMe peak of *NNN*-trimethylanilinium hexafluorophosphate (δ 3.62) was used as a standard in the latter solvent. Almost all the ^{13}C n.m.r. spectra were run on a Varian CFT20 spectrometer but, for greater accuracy, a Varian XL200 spectrometer was used for the measurement of $^{13}C^{15}N$ coupling constants (Table 1). The assignment of peaks in the ^{13}C spectra was based in part on the comparison of fully decoupled and partially decoupled spectra.

Reactions of NN,2,4,6-*Pentamethylaniline.*—The amine (0.1 g) and sodium nitrite (0.01 g) were added to aqueous nitric acid (70%; 1 cm^3) at 0 °C. After 1 h, the solution was added to a mixture of aqueous nitric acid (70%; 1 cm^3) and saturated aqueous potassium hexafluorophosphate (1 cm^3). The mixture was kept at 0 °C overnight; the *hexafluorophosphate* of the *ipso*-intermediate (2) had then precipitated as white flakes. These were filtered off, washed with water at 0 °C and with chloroform, and dried under vacuum. The product (60 mg) had m.p. 157—159 °C (decomp.) (Found: C, 37.3; H, 4.8; N, 8.0. $C_{11}H_{17}F_6N_2O_2P$ requires C, 37.3; H, 4.8; N, 7.9%).

A mixture of the amine (0.3 g), sodium nitrite (0.03 g), and 40% nitric acid (3 cm^3) was left at 0 °C overnight and then extracted with hexane. The extract, after being washed with dilute acid, dilute base, and water, was dried and evaporated to yield the dienone (4) (0.25 g). The ^1H n.m.r. spectrum [δ($CDCl_3$) 1.9 (3 H, s), 2.0 (6 H, s), and 6.86 (2 H, s)] and ^{13}C n.m.r. spectrum (Table 1) were identical with those of a synthetic sample (see text), but the nitrogen analysis was poor (Found: C, 59.9; H, 6.2; N, 8.9. Calc. for $C_9H_{11}NO_3$: C, 59.7; H, 6.1; N, 7.7%). Evaporation of a chloroform solution of the dienone (4) after 24 h gave mainly the phenol (5): this was purified on a silica gel column using light petroleum–methylene chloride–ethyl acetate (6 : 4 : 1) as eluant. The phenol (5) had m.p. 78—82 °C, δ($CDCl_3$) 2.2 (6 H, s), 5.26 (2 H, s), 7.03 (2 H, s), and variable (1 H, s) (Found: C, 59.4; H, 6.3; N, 8.2. Calc. for $C_9H_{11}NO_3$: C, 59.7; H, 6.1; N, 7.7%).

Reactions of NN,2,4-*Tetramethyl*-6-*nitroaniline.*—The nitration of this amine in 70% nitric acid and the precipitation of the hexafluorophosphate salt of the adduct (8) were carried out as described for the pentamethylaniline. The *salt* after being washed with iced water and ether had m.p. 108—110 °C (decomp.) (Found: C, 29.9; H, 4.1; N, 10.6. $C_{10}H_{15}F_6N_3O_5P$ requires C, 29.9; H, 3.8; N, 10.4%).

Reactions of NN,2,6-*Tetramethyl*-4-*methoxyaniline.*—The amine (0.1 g) was dissolved in aqueous nitric acid (51.6%; 1 cm^3) at 0 °C. After 1 h the mixture was poured into water at 0 °C and extracted with methylene chloride. After washing with dilute acid, dilute base, and water, the solvent was evaporated off and the quinone (14) purified by sublimation. The product had m.p. 71—72 °C (lit.,[16] 72—73 °C), δ_C($CDCl_3$) 188.2, 187.5 (C-1, C-4), 145.8 (C-2, C-6), 133.4 (C-3, C-5), and 16.0 p.p.m. (CH_3). The n.m.r. and i.r. spectra of the product were identical with those of a commercial sample of 2,6-dimethylbenzoquinone.

Acknowledgements

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