

*Compounds of Tertiary Amines with Nitrosyl Chloride and with
Dinitrogen Tetroxide.*

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Aliphatic and aromatic tertiary amines react with nitrosyl chloride and with dinitrogen tetroxide in inert solvents at -78° to give coloured addition compounds. That from trimethylamine and dinitrogen tetroxide has the formula $NMe_3 \cdot N_2O_4$, and that from dimethylaniline and nitrosyl chloride has the formula $NPhMe_2 \cdot NOCl$. By measurement of electrical conductances and absorption spectra the nitrosyl chloride and dinitrogen tetroxide complexes of dimethylaniline were shown to be the nitrosammonium salts $[NPhMe_2 \cdot NO]^+ X^-$ ($X^- = Cl^-$ or NO_3^-).

ALTHOUGH addition compounds of amines with oxides of nitrogen and related species have been postulated as intermediates in the reactions of amines with nitrosating agents (Donald and Reade, *J.*, 1935, 56; Crowley, Milton, Reade, and Todd, *J.*, 1940, 1288; Lamberton and Wright, *Canad. J. Res.*, 1948, 26, 110; Glazer, Hughes, Ingold, James, Jones, and Roberts, *J.*, 1950, 2671), little work has been directed towards their isolation. The addition compounds of tertiary amines would be expected to be more stable than those of other amines, and these alone have now been investigated.

Jones and Whalen (*J. Amer. Chem. Soc.*, 1925, 47, 1345) obtained an orange solid by mixing ethereal solutions of trimethylamine and nitrosyl chloride at -78° , which, on warming, became brown and then decomposed yielding nitric oxide, formaldehyde, trimethylammonium chloride, dimethylammonium chloride, and chloromethyl dimethylamine. These products are similar to those of the reaction between trimethylamine and hypochlorous acid (Meisenheimer, *Ber.*, 1913, 46, 1148). Dimethylaniline, with nitrosyl chloride, yields dimethyl-*p*-nitrosoaniline (Neber and Rauscher, *Annalen*, 1942, 550, 182); and with dinitrogen tetroxide yields a mixture of nitroso- and nitro-compounds (Schaarschmidt, Balzerkiewicz, and Gante, *Ber.*, 1925, 58, 499). Battagay and Kern (*Bull. Soc. chim.*, 1928, 43, 114) found that when the latter reaction was carried out in benzene solution below 10° the mixture was initially brown and then rapidly became green.

Since our work was completed, Sisler, Burkhardt, and Davenport (*J. Amer. Chem. Soc.*, 1953, 75, 4175) have reported addition compounds of dinitrogen tetroxide with heterocyclic amines and with triethylamine; and Addison, Hodge, and Sheldon (*Chem. and Ind.*, 1953, 1338) have commented on the difference between the formulæ of the complexes obtained by these workers and those obtained in the present work, as described in a preliminary note (Comyns, *Nature*, 1953, 172, 491).

Earlier work on reactions between pyridine and oxides of nitrogen includes Spencer's claim (*Chem. News*, 1903, 87, 176) to have isolated a white addition product with dinitrogen tetroxide; Schaarschmidt *et al.* (*loc. cit.*) stated that the already known addition product with dinitrogen tetroxide did not rearrange to give 3-nitropyridine; Shorigen and Topschiew (*Ber.*, 1936, 69, 1874), studied gas-phase reactions of pyridine with dinitrogen tetroxide and obtained 3-nitropyridine and pyridinium nitrate; and Haines and Adkins (*J. Amer. Chem. Soc.*, 1925, 47, 1419) isolated an addition compound with dinitrogen pentoxide, which, however, might have been pyridinium nitrate (Haines, Thesis, Wisconsin, 1924, p. 15).

EXPERIMENTAL

Materials.—Dinitrogen tetroxide was prepared by dropping fuming nitric acid on damp sodium nitrite, and distilling the product over phosphoric oxide in a stream of oxygen until it gave a white solid on cooling. Nitrosyl chloride was prepared by the method of *Inorg. Synth.*, 1939, 1, 53, and freed from hydrogen chloride by prolonged refluxing in a current of nitrogen. Trimethylamine was refluxed with acetic anhydride and then distilled through a tube packed with mercuric oxide and barium oxide. Triethylamine was distilled from barium oxide. Dimethylaniline, refluxed with acetic anhydride and fractionated, had b. p. $192-193^{\circ}$, n_D^{25} 1.5556. Dimethyl-*o*-toluidine (B.D.H.) was purified by von Braun and Aust's method (*Ber.*, 1914, 47,

260); the two fractions collected in the final distillation had n_D^{25} 1.5230 (cf. n_D^{20} 1.5153 given by von Braun *et al.*, *loc. cit.*, and n_D^{20} 1.5255 by Ley and Pfeiffer, *Ber.*, 1921, 54, 371). Dimethylmesidine was synthesised from mesitylene by nitration, reduction, and methylation, and the crude product was refluxed with acetic anhydride: fractionation yielded a product of b. p. 212—213°. Diethylaniline and *N*-methyldiphenylamine were dried over potassium hydroxide, and distilled under reduced pressure. The three dimethylnitroanilines and dimethyl-*p*-nitrosoaniline were kindly supplied by Dr. E. L. Blackall. Pentane was prepared from "standard pentane" by treatment with nitrating acid for two months, followed by alkaline permanganate; after drying (P_2O_5), the product was fractionated and the fraction of b. p. $< 40^\circ$ was collected. *s*-Tetrachloroethane was dried ($CaCl_2$) and distilled under reduced pressure. Ethyl chloride and methylene chloride were dried (P_2O_5) and distilled. Acetonitrile was dried (K_2CO_3) and fractionated, it had b. p. 81.0—81.3°/744 mm., n_D^{25} 1.3422.

Introductory Experiments.—Solutions of the reactants in corked test-tubes were cooled in solid carbon dioxide and alcohol and then mixed. Some of the experiments on the trimethylamine-dinitrogen tetroxide system were performed in an all-glass system with rigid exclusion of moisture, and results identical with those of similar experiments in test-tubes were obtained.

Dinitrogen tetroxide solutions in ether and in pentane, when mixed at -78° with solutions of trimethylamine and triethylamine in excess, gave pale yellow precipitates and solutions. When the mixtures were warmed to *ca.* -55° the precipitates became brown, and further warming caused the colour completely to fade and nitric oxide to be evolved. Trimethylamine and triethylamine, treated with an excess of dinitrogen tetroxide in ether at -78° , gave yellow products similar to those produced when the amine was present in excess, but on warming to *ca.* -55° the precipitates became more dense and assumed a flesh colour. These new precipitates were relatively stable and began to decompose at *ca.* -5° , evolving oxides of nitrogen and leaving cream-coloured solids. Our attention to these reactions in the presence of excess of dinitrogen tetroxide was first drawn by the work of Sisler *et al.* (*loc. cit.*), and we therefore did not further examine the flesh-coloured precipitates.

Some of the white solid produced by the reaction of dinitrogen tetroxide with trimethylamine in excess was prepared in an all-glass system in order to exclude moisture. Trimethylamine (0.36 g. in 5 ml.) and dinitrogen tetroxide (0.28 g. in 5 ml.) were mixed in carbon tetrachloride at *ca.* -25° : a gelatinous brown solid resembling precipitated ferric hydroxide was produced. This solid was filtered off and washed with cold carbon tetrachloride while still at *ca.* -25° by means of a sintered-glass disc in the base of the reaction tube which was immersed in the cold bath. The filtrate and washings required 12.1 ml. of 0.107*N*-sulphuric acid for neutralisation. The remaining brown solid was allowed to warm slowly to room temperature: nitric oxide was evolved and a sticky, deliquescent, white solid (0.33 g.) remained. Recrystallisation *in situ* from dry acetonitrile yielded crystals of m. p. 130° which were not deliquescent; a second recrystallisation yielded crystals of m. p. 153° , mixed m. p. with trimethylammonium nitrate 153° . By analogy with the work of Jones and Whalen (*loc. cit.*) the deliquescent component of the crude white solid was probable dimethylammonium nitrate.

Dimethylaniline, diethylaniline, dimethyl-*p*-nitrosoaniline, and *N*-methyldiphenylamine reacted with nitrosyl chloride and with dinitrogen tetroxide solutions at -78° to give complexes of a very intense dark red colour, which were soluble in halogenated hydrocarbons (*e.g.*, ethyl chloride, methylene chloride, *s*-tetrachloroethane-ether), but sparingly soluble in hydrocarbons and in ether. These complexes were more stable than those of the aliphatic amines, and could be kept for several hours at -78° without visible change. When the complex of dimethylaniline with nitrosyl chloride was warmed above -78° its red colour was replaced by the green colour of dimethyl-*p*-nitrosoaniline. When solutions of nitrosyl chloride and dimethylaniline were mixed at room temperature a transient red colour was observed before the green colour appeared.

Dimethylmesidine gave yellow complexes with nitrosyl chloride and with dinitrogen tetroxide at -78° , resembling those of the aliphatic amines. Their colour faded on slight warming, nitric oxide was evolved, and white solid remained. The solid from the nitrosyl chloride complex was recrystallised from acetonitrile and yielded dimethylmesidinium chloride, m. p. 153 — 155° , picrate, m. p. 181 — 183° , [Emerson *et al.* (*J. Amer. Chem. Soc.*, 1941, 63, 972) give m. p. 155 — 156° , picrate, m. p. 181 — 182°].

Dimethyl-*o*-toluidine gave a vermilion precipitate with a solution of nitrosyl chloride in ether at -78° . On slight warming, the colour faded to orange, and nitric oxide was evolved, but on cooling again to -78° the vermilion colour reappeared. This process was repeated several times until the vermilion colour failed to reappear on cooling. This amine was the only one of those examined to show this reversible colour change.

There was no visible reaction between solutions of the three dimethylnitroanilines and nitrosyl chloride or dinitrogen tetroxide at -78° .

Combining Ratios.—The molecular ratios in which the reactants had combined in two of the complexes were determined as follows. Known quantities of the two reactants were mixed at -78° or -100° in pentane, and that in excess was quantitatively removed by high-vacuum distillation through a short-path apparatus into a trap cooled in liquid air, the reaction vessel being kept at -78° or -100° . The excess, which had collected in the liquid-air trap, was then determined. The two systems studied by this method were that of dinitrogen tetroxide with trimethylamine in excess, and of dimethylaniline with nitrosyl chloride in excess.

Trimethylamine-dinitrogen tetroxide. The solution of trimethylamine was stored in, and delivered from, an automatic pipette fitted with a jacket containing ice and water. It was standardised by delivering aliquot parts into an excess of hydrochloric acid and back-titration with standard alkali (methyl-red). The dinitrogen tetroxide solutions were standardised by Milligan's method (*J. Phys. Chem.*, 1924, **28**, 554); 2-ml. aliquot parts were pipetted into concentrated sulphuric acid (5 ml.) contained in a small stoppered flask cooled in ice, and the mixture was gently agitated until the brown fumes had disappeared. The solution was then poured into potassium permanganate solution (100 ml. of *ca.* 0.05N) with rapid stirring, the flask was washed twice with sulphuric acid, and the washings were added to the solution. An excess of ferrous sulphate solution was then added and the excess determined by titration with permanganate. In the distillation experiments 5-ml. aliquot parts of the amine solution were delivered into the reaction vessel (a 1" test-tube with a B29 socket) cooled to -100° : this temperature was attained by cooling a solid carbon dioxide-ethanol bath by liquid air contained in a small metal pot. The dinitrogen tetroxide solution (2 ml.) was added slowly with gentle shaking; it was allowed to run down the cold walls of the reaction vessel before meeting the amine solution. With continuous evacuation by a mercury-vapour diffusion pump about 30 min. sufficed for all of the solvent and the trimethylamine in excess to have distilled into the receiver (a 2" test-tube made from a B55 socket). The complex was left adhering to the walls of the reaction tube as a dry, brown powder which rapidly became white after removal of the cold bath. The distillate was pale yellow, showing that some volatilisation of dinitrogen tetroxide had occurred. The amine in the distillate was determined by absorption into hydrochloric acid and back-titration with alkali: the error due to the presence of the small amount of dinitrogen tetroxide was probably negligible. The results are given in Table 1. There is considerable scatter in the values for the combining ratio, but

TABLE 1. *Trimethylamine with dinitrogen tetroxide.*

N_2O_4 taken	NMe_3 taken	NMe_3 recovered	Initial ratio	Final ratio	N_2O_4 taken	NMe_3 taken	NMe_3 recovered	Initial ratio	Final ratio
0.00	10.6	10.5	—	—	1.88	3.63	1.49	1.9	1.14
5.81	8.75	3.60	1.5	0.89	1.92	4.02	2.24	2.1	0.92
3.59	5.47	2.11	1.5	0.94	1.46	5.13	3.59	2.9	1.05
5.61	8.50	3.00	1.5	0.98					

Quantities are expressed in moles $\times 10^{-3}$. "Ratio" refers to mole ratio $NMe_3:N_2O_4$.

these are fairly evenly distributed about unity, and we conclude that the compound $NMe_3 \cdot N_2O_4$ is formed at -100° . It would have been desirable to have repeated the experiments but with dinitrogen tetroxide in excess: this was not attempted as the simple apparatus employed was unsuitable for the quantitative absorption of dinitrogen tetroxide.

Dimethylaniline-nitrosyl chloride. The nitrosyl chloride solutions were stored in and delivered from the cooled automatic pipette. They were standardised by absorption into sodium hydroxide solution at 0° , and Volhard titration of the chloride ion thereby produced. Dimethylaniline was delivered from a weight pipette into the reaction tube, solvent was added, and the solution was cooled to -78° . The distillation procedure was similar to that described above. At the conclusion of a distillation the receiver was removed, silver nitrate solution was added, and a bung was quickly inserted into the neck. On warming to room temperature, the nitrosyl chloride reacted with the melting silver nitrate solution, and the remaining silver nitrate was then determined by thiocyanate titration. The results are given in Table 2. They show that with pentane as solvent a 1:1 complex is formed, but that with ethyl chloride and methylene chloride less than one equivalent of nitrosyl chloride remains with the dimethylaniline. Continued pumping of the solid after all of the solvent had been removed did not result in the removal of any more nitrosyl chloride. If, however, solvent was continually added as it distilled out and the mixture was never allowed to become dry, nitrosyl chloride could continuously be removed: this was the method by which the value of 0.52 was obtained for the

combining ratio in ethyl chloride, and 0.91 in pentane. Pure solid nitrosyl chloride can rapidly be removed under these conditions and so could not have been present as such in the remaining red solids. The red solids rapidly became green after removal of the cold bath.

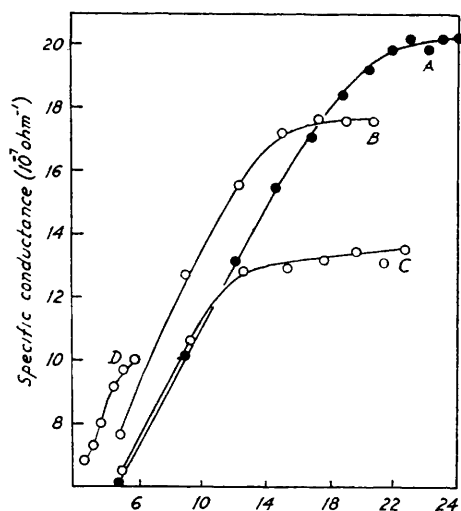
TABLE 2. *Dimethylaniline with nitrosyl chloride.*

NPhMe ₂ taken	NOCl taken	NOCl recovered	Initial ratio	Final ratio	Solvent	Volume of solvent (ml.)
0.00	2.28	2.26	—	—	C ₅ H ₁₂	5
1.21	2.12	0.84	1.75	1.06	"	10
1.59	2.42	0.68	1.53	1.09	"	10
1.21	2.31	1.03	1.88	1.06	"	10
1.18	2.27	1.09	1.92	1.00	"	17
1.19	2.14	1.06	1.80	0.91	"	20
1.41	2.48	1.25	1.75	0.87	C ₂ H ₅ Cl	10
1.03	2.43	1.65	2.36	0.76	"	10
1.20	2.42	1.80	2.02	0.52	"	20
1.83	2.92	1.23	1.60	0.92	CH ₂ Cl ₂	10
1.85	2.88	1.17	1.55	0.92	"	10

Quantities are expressed in moles $\times 10^{-3}$. "Ratio" refers to mole ratio NOCl : NPhMe₂.

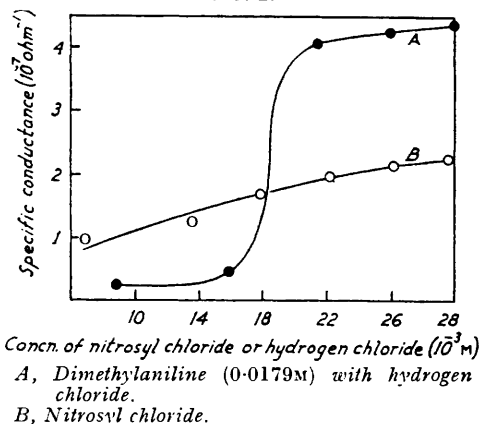
Measurements of Electrical Conductance.—Conductance measurements were made on the system dimethylaniline–nitrosyl chloride and related systems at -78° , and the results are shown in Figs. 1 and 2. The solvent was prepared by diluting *s*-tetrachloroethane (170 ml.) with ether to 250 ml. As much heat is liberated on mixing, the final few ml. of ether were not added until

FIG. 1.



Concn. of nitrosyl chloride or trimethylanilinium iodide (10^3 M)
A, B, C, Dimethylaniline (0.0216, 0.0158, 0.0110M respectively) with nitrosyl chloride.
D, Trimethylanilinium iodide.

FIG. 2.



Concn. of nitrosyl chloride or hydrogen chloride (10^3 M)
A, Dimethylaniline (0.0179M) with hydrogen chloride.
B, Nitrosyl chloride.

the bulk of the mixture had re-attained room temperature. A correction was applied for the contraction of the solvent on cooling from 0° or 20° , at which the solutions were prepared or standardised, to -78° : Dr. I. G. Ross of this Department found that 1 ml. at 20° occupied 0.903 ml. at -78° , and that 1 ml. at 0° occupied 0.922 ml. at -78° . All measurements were made by using as a thermostat a Dewar vessel containing a stirred slurry of solid carbon dioxide and ethanol, the temperature of which was found to vary from -78° to -80° . The cell was similar to the Shedlovsky pattern, constructed from a 100-ml. flask attached by a capillary tube to the electrode compartment of 5 ml. capacity. The electrodes were parallel plates of bright platinum. The cell-constant was measured at 0° , with $n/100$ -potassium chloride solution as the standard, and found to be 0.186 cm^{-1} . This value was used without correction for calculating specific conductances at -78° . Measurements of resistance lower than $3 \times 10^5 \text{ ohm}$ were made on an

A.C. bridge at 1000 c.p.s. Measurements of resistance higher than this were made on a D.C. bridge incorporating a 6-valve amplifier, constructed by Mr. B. Eisler of this Department.

(a) *Trimethylanilinium iodide*. A solution was prepared containing 0.35 g. of the crystalline salt, m. p. 235° (decomp.), in 25 ml. of solution, and 15 ml. of this were delivered into the cell. Conductance measurements were made on this solution and after successive dilutions by solvent.

(b) *Nitrosyl chloride*. The cell initially contained solvent (12 ml.), and aliquot parts of nitrosyl chloride solution (1 ml. of 0.0823M at 0°) were successively added. The conductance observed may have been due to the ionisation $\text{NOCl} \rightleftharpoons \text{NO}^+ \text{Cl}^-$, but as great care was not taken in purifying the solvent the measurements are of little quantitative significance. The specific conductance at 0.02M was $1.8 \times 10^{-7} \text{ ohm}^{-1}$, which may be compared with the value of $6 \times 10^{-7} \text{ ohm}^{-1}$ found by Seel (*Z. anorg. Chem.*, 1944, 252, 39) for a solution of nitrosyl chloride of this concentration in sulphur dioxide at -70° .

(c) *Dimethylaniline-nitrosyl chloride*. In each of three experiments the amine concentration was kept constant while that of the nitrosyl chloride increased and measurements were made at different nitrosyl chloride concentrations. These conditions were obtained by the following procedure. Two amine solutions were prepared, one of exactly twice the concentration of the other, and the more dilute solution was contained in the conductance cell. The nitrosyl chloride solution was added to this in 1-ml. aliquot parts, as also was the more concentrated amine solution. In one experiment dimethylaniline solution (7.5 ml., containing 0.0615 g. to 25 ml.) and solvent (7.5 ml.) were delivered into the cell and successive additions made of both nitrosyl chloride solution (0.0823M at 0°) and amine solution. The conductance of the dimethylaniline solutions rose sharply with increase in nitrosyl chloride concentration until equivalent quantities were present, and then remained nearly constant. It would probably have continued to rise slowly were it not for the simultaneous slow decomposition of the complex, which process causes a fall in conductance.

(d) *Dimethylaniline-hydrogen chloride*. The procedure was similar to that used with nitrosyl chloride. The conductance of the dimethylanilinium chloride formed under these conditions was much smaller than that of the dimethylaniline-nitrosyl chloride complex. The greater conducting power of quaternary ammonium salts over those containing a bound proton is familiar (cf., e.g., Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, 55, 21).

Absorption Spectra.—Qualitative observations were made of the absorption spectra of dimethylaniline solutions with added nitrosyl chloride and dinitrogen tetroxide. The solvent was the same *s*-tetrachloroethane-ether as was used for the conductance measurements. The solutions were prepared and kept at -78° , and measurements were made with a Cary recording spectrophotometer.—I am indebted to Dr. R. Passerini for them. The cell was designed by Dr. I. G. Ross. It had a continuously evacuated outer jacket of stainless steel, enclosing the two brass cells surrounded by coolant. Amine was present in excess in both experiments, and the spectrophotometer recorded the difference in the absorption between the amine solution and a similar solution containing added nitrosyl chloride or dinitrogen tetroxide. Similar spectra were obtained whether nitrosyl chloride or dinitrogen tetroxide was employed: the solution containing nitrosyl chloride exhibited a sharp maximum at 398 m μ and that containing dinitrogen tetroxide gave a similar maximum at 404 m μ . These results indicate that the same species is responsible for the colour of both solutions. Addison *et al.* (*loc. cit.*) have pointed out that the complex of dinitrogen tetroxide with diethylnitrosamine also has an absorption maximum in this region (at 412 m μ).

DISCUSSION

The analytical results show that dimethylaniline and nitrosyl chloride form a 1 : 1 addition compound at -78° , and the similarity of the electrical conductance of this adduct to that of a uni-univalent quaternary ammonium salt indicates that it is the nitrosammonium salt $[\text{NPhMe}_2\text{NO}]^+\text{Cl}^-$. The similarity between the absorption spectra of the nitrosyl chloride and the dinitrogen tetroxide adduct of dimethylaniline indicates that the latter adduct has the analogous formula $[\text{NPhMe}_2\text{NO}]^+\text{NO}_3^-$.

The fact that the combining ratio of nitrosyl chloride to dimethylaniline, as measured in the analytical experiments, was less than unity when halogenated solvents, in which the complex is soluble, were employed in place of pentane, in which the complex is sparingly soluble, indicates that an equilibrium may exist in solution :



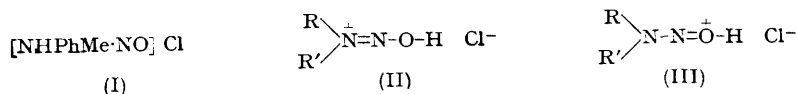
An alternative explanation is that solid complexes containing less than one molecule of nitrosyl chloride to one of dimethylaniline are formed under these conditions.

The decomposition products of the complexes of the aromatic amines were not examined in detail, but are probably identical with the products obtained when the reactants are mixed at room temperature. The complexes of the aliphatic amines and of dimethylmesidine, which in many ways resembles an aliphatic amine, are much less stable than those of the aromatic amines; and their decomposition products correspond closely with those predicted by Ingold *et al.* (*loc. cit.*) for the nitrosammonium ions which were postulated as intermediates in the oxidative de-alkylation of aromatic amines during nitrosation and nitration.

The reversible phenomena encountered in the dimethyl-*o*-toluidine-nitrosyl chloride system may be explained by the low reactivity of this amine toward nitrosating agents. Dimethyl-*o*-toluidine, as is well known (*cf.*, *e.g.*, von Braun, Arkuszewski, and Kohler, *Ber.*, 1918, **51**, 282), is resistant to nuclear nitrosation. It is usually supposed, therefore, that it is inactive toward nitrous acid (Hickinbottom, "Reactions of Organic Compounds," Longmans, London, 1948, p. 318), but it has been found (unpublished results) that products analogous to those produced by the action of nitrous acid on dimethyl-*p*-toluidine (Crowley *et al.*, *loc. cit.*) are formed, although at a much slower rate than nuclear nitroso-compounds are formed by related amines.

The substances prepared by Sisler *et al.* (*loc. cit.*) from dinitrogen tetroxide and triethylamine have properties different from those of the compounds obtained in the present work. Our observation that pink substances are formed from trimethylamine and triethylamine in the presence of an excess of dinitrogen tetroxide, at about the temperature at which the initial yellow complexes decompose, suggests that the substances analysed by Sisler *et al.* might not have been simple addition compounds but were more complex substances produced by reactions between dinitrogen tetroxide and the decomposition products of the addition compounds. Addison and Hodge (*Chem. and Ind.*, 1953, 1315) have obtained the yellow compound $N_2O_4 \cdot 2(Et_3NH \cdot NO_2) \cdot 4Et_2O$ which, they point out, is closely related to one of the substances obtained by Sisler *et al.* The analytical procedure used by Sisler *et al.* could not be used for the complexes which we, and Jones and Whalen, obtained, since in this procedure the reaction mixture warms to a temperature considerably above -75° during the filtration, and extensive decomposition with loss of nitric oxide would occur.

The hydrochloride of methylphenylnitrosamine has been formulated as the nitrosammonium salt (I) (Neber and Rauscher, *loc. cit.*), but as this and other nitrosamine hydrochlorides are relatively stable substances and unlike the complexes obtained in the present work it seems unlikely that they have similar formulæ. It is therefore suggested that in the nitrosamine hydrochlorides the protons are attached to the oxygen atoms, and that resonance between structures (II) and (III) occurs:



A substance (II) is isoelectronic with a ketone oxime, and similarities would therefore be expected between the infrared spectra of nitrosamine hydrochlorides and ketone oximes with similar alkyl groups.

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