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CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
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Reactions of Nitrogen(II) Oxide with Miscellaneous Lewis Bases

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Our previous studies of reactions of nitrogen(II) oxide with primary and secondary amines have been extended to reactions of trimethylamine, diamines, aromatic and aliphatic sulfides and thiols, phosphines, phosphites, triphenylarsine, triphenylstibine, and sodium phenoxide. N_2O_2 adducts are formed with the amines. In the presence of strong bases, mercaptans are converted to disulfides in good yields. Triphenylphosphine and triethylphosphite were converted to the phosphine oxide and phosphate, respectively. Starting materials were recovered when reaction was attempted under the reported conditions with triphenylarsine, triphenylstibine, dialkyl sulfides, thiophene, or sodium phenoxide.

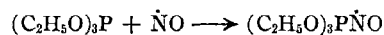
Introduction

The reaction of nitric oxide with sulfite ion² and with various primary and secondary amines^{3,4} produces: $SO_3N_2O_2^{-2}$, $RNH_3^+RNHN_2O_2^-$, and $R_2NH_2^+R_2NN_2O_2^-$, respectively. It was of interest to study the reaction of nitrogen(II) oxide with tertiary amines, diamines, and other group V and VI donors.

Trimethylamine on reaction with nitric oxide gives rise to the very unstable product $(CH_3)_3NN_2O_2$. Solids of moderate stability are isolated from the reaction of piperazine and N,N' -dimethylethylenediamine with nitric oxide.

In studies of sulfur and phosphorus donors as well as triphenylarsine, triphenylstibine, and sodium phenoxide, we were not able to isolate products containing nitrogen. In cases where reaction occurs, products arising from the "oxidizing" nature of nitric oxide are produced. Aliphatic and aromatic mercaptans in the presence of sodium methoxide produce disulfides, whereas triphenylphosphine is converted to triphenylphosphine oxide and triethylphosphite to triethylphosphate. Some of the above oxidations are convenient synthetic procedures that

yield products of high purity directly. The kinetics for the reaction of nitric oxide with triethylphosphite have been studied.⁵ The results indicate that the first step is rate controlling and is represented by the equation



Experimental

Purification of Materials.—Matheson commercial grade nitric oxide may be used directly. Eastman Kodak or Pitt-Consol freshly distilled liquids or dry recrystallized solids were used as starting materials. Triethylphosphite was distilled from anhydrous BaO.

Instrumentation.—Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. The instrument was frequency calibrated using the absorptions of ammonia, water vapor, and polystyrene, and the appropriate corrections were applied to the spectral data reported.

General Procedure for Sulfur Compounds.—Equimolar quantities of mercaptan and freshly prepared sodium methoxide are dissolved in methanol, placed in an air-tight three-neck flask, and cooled to ice bath temperature. The procedure employed is that previously described³ as the atmospheric pressure method. The products are either white or light yellow solids which precipitate from solution after 20 to 30 min., or clear light yellow liquids which are distilled from the reaction mixture. The solids are conveniently recrystallized from methanol or hexane. Products obtained from the corresponding mercaptans are listed in Table I. Boiling points, melting points, and spectra agree with reported data.

(1) Abstracted in part from the Ph.D. theses of R. Longhi, University of Illinois, 1962, and R. E. Ragsdale, (1960).

(2) R. S. Drago, *J. Am. Chem. Soc.*, **79**, 2049 (1957) and references cited therein.

(3) R. S. Drago and F. E. Paulik, *ibid.*, **82**, 96 (1961).

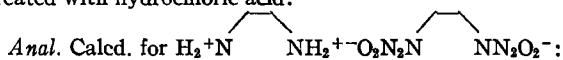
(4) R. S. Drago and B. R. Karstetter, *ibid.*, **83**, 1819 (1961).

(5) L. P. Kuhn, J. O. Doali, and C. Wellman, *ibid.*, **82**, 4792 (1960). This article appeared after our phosphorus work.

General Procedure for Phosphorus Compounds.—

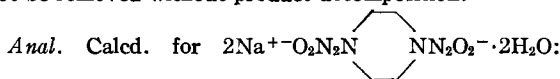
The starting material (phosphine or phosphite) is dissolved in anhydrous diethyl ether and placed in a three-neck flask similar to that used for the sulfur compounds. The system is cooled in an ice bath, flushed with pure, dry nitrogen, and saturated with nitric oxide (treated in the same way as described for the sulfur compounds) for 24 hr. When triphenylphosphine is used as a starting material the white solid triphenylphosphine oxide starts to precipitate in about 30 min. When the reaction is complete, the white solid product is filtered, washed with anhydrous diethyl ether, and vacuum-dried over anhydrous phosphorus pentoxide. In the conversion of triethylphosphite to triethylphosphate, the colorless liquid product is vacuum-distilled directly from the reaction mixture. The results obtained for these reactions are listed in Table II.

Piperazine.—Seven g. of piperazine dissolved in 25 ml. of absolute methanol was drawn into an evacuated autoclave. The solution was saturated with nitric oxide for 24 hr. at -78° according to the high pressure technique previously described.⁴ At the end of the reaction period a white solid is precipitated from solution by the addition of anhydrous diethyl ether. This material is no longer soluble in cold methanol and it is purified by repeated grinding of the solid in cold methanol and then filtering the precipitate. The white solid product melts at 88° in an open tube, and evolves nitric oxide when treated with hydrochloric acid.



C, 32.9; H, 6.9; N, 38.3. Found: C, 32.9; H, 6.8; N, 36.8.

The sodium salt of this material was prepared by using the high pressure technique at -78° . Seven and one-half g. of piperazine in 50 ml. of absolute methanol containing 7 g. of sodium hydroxide was allowed to react for 12 hr. At the end of this period the reaction mixture was filtered to yield a white solid, which was washed with cold methanol and anhydrous diethyl ether, and then vacuum-dried over anhydrous phosphorus pentoxide. This material evolves nitric oxide when treated with hydrochloric acid and although it is quite stable at room temperature, it explodes at 210° in an open melting tube. Although this sodium salt is a fine, white crystalline material and does not appear wet, the infrared spectrum of a Nujol mull shows the presence of water. This is in contrast to the alkyl ammonium salt. Elemental analysis indicates a dihydrate, and the solvate molecules cannot be removed without product decomposition.



C, 16.79; H, 4.23; N, 29.37. Found: C, 16.61; H, 4.07; N, 29.37.

N,N'-Dimethylethylenediamine.—Fifteen ml. of anhydrous N,N'-dimethylethylenediamine in 60 ml. of anhydrous diethyl ether was drawn into an evacuated autoclave and the solution was saturated with nitric oxide for 12 hr. at -78° , according to the high pressure technique.⁴ At the end of the reaction period the white solid product was filtered, washed with anhydrous diethyl ether, and vacuum-dried over anhydrous phosphorus pentoxide. The compound is insoluble in chloroform and low molecular weight alcohols, but dissolves in water with

TABLE I

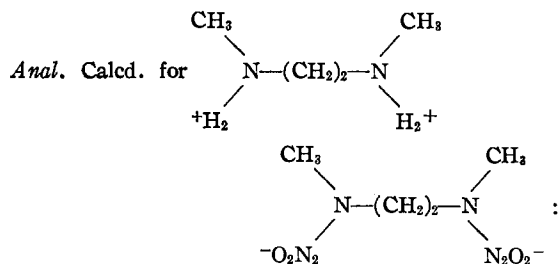
Compound	% Yield	Calcd. % C	Found % C	Calcd. % H	Found % H
(C ₂ H ₅ -S-) ₂	83	39.28	39.51	8.27	8.35
(CH ₃ (-CH ₂) ₅ -S-) ₂	84	61.47	61.61	11.17	11.25
(CH ₃ (-CH ₂) ₁₁ -S-) ₂	88	71.57	71.29	12.51	12.62
(C ₆ H ₅ -S-) ₂	92	66.01	65.88	4.62	4.57
(<i>p</i> -C ₆ H ₄ -C ₆ H ₄ -S-) ₂	91	72.67	72.32	7.93	8.04
(β -Naphthyl-S-) ₂	88	75.44	75.06	4.43	4.42

TABLE II

Compound	% yield ^a	Calcd. % C	Found % C	Calcd. % H	Found % H
(C ₂ H ₅ O) ₃ PO	73	39.57	39.72	8.29	8.45
(C ₆ H ₅) ₃ PO	98	77.68	77.79	5.43	5.38

^a Yields refer to the amount of analyzed products obtained.

decomposition. Elemental analyses on the crude material are poor, but when the compound is washed with methanol and ether and dried over P₂O₅, satisfactory analytical data are obtained. The white solid product is fairly stable at room temperature, melts at 91 – 92° in an open tube, and evolves nitric oxide when treated with hydrochloric acid.



C, 32.4; H, 8.2; N, 37.8. Found: C, 32.7; H, 8.3; N, 36.8.

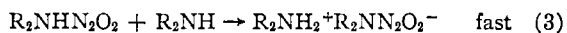
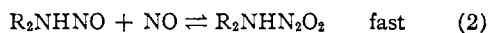
Trimethylamine.—The reaction of trimethylamine and nitric oxide was carried out at -78° using the atmospheric pressure method.⁸ Nitric oxide was passed over the well stirred pure amine for 4 days. The flask was flushed with nitrogen and warmed to allow evaporation of the amine until a slurry remained. The flask was transferred to a drybox and the slurry was filtered cold and washed with cold diethyl ether. The solid then was transferred to a sample vial and stored over Dry Ice. The compound decomposes on warming to room temperature. Elemental analyses were obtained by loading a weighed sample tube with the cold product in the drybox, sealing the tube in a flame, and breaking the weighed sample in the combustion train.

Anal. Calcd. for (CH₃)₃NN₂O₂: C, 30.25; H, 7.61. Found: C, 30.34; H, 9.31.

The analysis for hydrogen is high because the large amount of NO₂ which formed in the train probably was absorbed by water which was weighed to give the hydrogen analysis. The compound also was analyzed by a Kjeldahl type procedure. The addition compound was loaded into a sealed tube and broken under concentrated sodium hydroxide. The amount of amine which was distilled into boric acid and titrated agreed within 3% of the value expected theoretically for (CH₃)₃NN₂O₂.

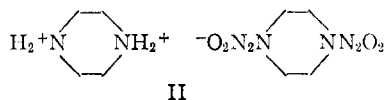
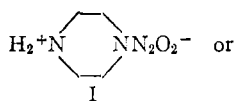
Discussion

By analogy with the phosphite reaction, the following mechanism is proposed for the reaction of amine and nitric oxide



Since trimethylamine cannot undergo the third step of this reaction series it was of interest to attempt the preparation of the addition compound. The very unstable compound obtained has an elemental analysis in agreement with the formula $(CH_3)_3NN_2O_2$. Attempts to produce similar addition compounds with pyridine, α - and γ -picoline, and 2,6-lutidine were unsuccessful. Evidently, a strong donor is required to form these adducts and since the addition compounds are not ionic like the salts obtained from the primary and secondary amine reaction, there is less contribution to the stability of the addition compounds from crystal lattice energies.

Both piperazine and N,N'-dimethylethylenediamine form salts with nitrogen(II) oxide. The product of the piperazine reaction can be formulated as either



A sodium salt derivative was prepared, with the empirical formula $Na_2O_2N_2N$ $NN_2O_2 \cdot H_2O$, supporting structure II. Attempts to prepare a sodium salt from the product of the N,N'-dimethylethylenediamine reaction were not successful, so the structural analogy with that formulated for the piperazine product could not be confirmed.

Essentially a quantitative yield (98%) of triphenylphosphine oxide is produced from the reaction of triphenylphosphine and nitric oxide. This reaction is of synthetic value since the reac-

tion product is obtained directly in a high degree of purity. Triethylphosphite is oxidized to the phosphate, in 73% yield. Under different experimental conditions, Kuhn and co-workers⁵ have prepared the phosphate in 100% yield from the phosphite and nitric oxide. In contrast to the above reactions, triphenylphosphite could not be converted to triphenylphosphate under our reaction conditions either at room temperature, 0°, or -78° in anhydrous diethyl ether. Both the high pressure technique⁴ and atmospheric pressure methods³ were attempted. This can be explained if the formation of an intermediate, R_3PNO , is assumed to be the first step in the reaction. This has been demonstrated for $(C_2H_5O)_3P$. The weaker basicity of $(C_6H_5O)_3P$ reduces the tendency of this compound to undergo the initial step in the reaction, and oxidation does not occur.

The reaction of nitrogen(II) oxide with mercaptans in the presence of sodium methoxide in methanol solution under pure, dry nitrogen appears to be a general technique for the preparation of aliphatic and aromatic symmetrical disulfides. We were unable to prepare unsymmetrical disulfides by this method, but this fact is not surprising since recent studies of disproportionation reactions between unsymmetrical disulfides show the equilibrium to be in favor of the symmetrical compounds.^{6,7}

Under the conditions employed there is no reaction between nitric oxide and symmetrical sulfides, and neither sulfoxides nor sulfones are produced. Products were not obtained from the reaction of nitric oxide with thiophene in the presence or absence of sodium methoxide in either methanol or anhydrous diethyl ether at room temperature, 0°, or -78°.

Acknowledgments.—The authors wish to express their appreciation to the U. S. Army Research Office (Durham) for financial support of this research under Grant No. USDA-G-72.

(6) L. Haraldson, C. J. Olander, S. Sunner, and E. Varde, *Acta Chem. Scand.*, **14**, 1507 (1960).

(7) R. G. Hiskey and F. I. Carroll, *J. Am. Chem. Soc.*, **83**, 4644 (1961).