sulfonium fluorenylides led to the liberation of the original sulfide along with the formation of a carbene dimer. Dimethylsulfonium dicyanomethylide (I) starts decompositing at 190° and undergoes a vigorous, self-sustaining degradation at 230°. The predicted dimethyl sulfide and tetracyanoethylene are among the products, but in addition at least six other gaseous, liquid, and solid products have been trapped. The course of this decomposition and a fuller exposition of the degradation products will be the subject of a future paper.

Experimental[12]

Dimethylsulfonium Dicyanomethylide (Method A).—A 250-ml. three-neck flask fitted with a reflux condenser, thermometer, stirrer, and dropping funnel was charged with 44 g. (0.66 mole) of malononitrile, 52 g. (0.66 mole) of dimethyl sulfoxide, and 85 ml. of methylene chloride. The mixture was cooled to 10–15°, and 80 g. (0.66 mole) of thionyl chloride was added dropwise over a period of 45 min., maintaining the temperature between 15–20°. When one-half of the thionyl chloride had been added, a bright yellow precipitate began to form. When the addition was complete, the ice bath was removed and the reaction mixture was allowed to warm to room temperature and filtered. The solid was washed with several small portions of methylene chloride, then dried to give 56.6 g. (68%) of the dihydrochloride. Free sulfonium dicyanomethylide was obtained by dissolving the salt in a minimum of hot water and adding sodium bicarbonate until the solution became slightly basic. The aqueous layer was extracted with several portions of methylene chloride, which was combined, dried over magnesium sulfate, and stripped under vacuum to give 22 g. (60%) of crude yellow ylide. White prisms, m.p. 99–100°, were obtained on recrystallization from 2-propanol.

Anal. Calcd. for $C_5H_8Cl_2N_2S$ (dihydrochloride salt): C, 30.17; H, 4.02; Cl, 35.63. Found: C, 29.66; H, 4.18; Cl, 35.03.

Dimethylsulfonium Dicyanomethylide (Method B).—A solution of 3.0 g. (0.048 mole) of dimethyl sulfide in 15 ml. of chloroform was added rapidly to a solution of 7.0 g. (0.048 mole) of bromomalononitrile in 15 ml. of chloroform. The clear solution was stirred with a magnetic stirrer in a 50-ml. round-bottom flask overnight. The yellow precipitate was filtered, washed with cold chloroform, and dried. A yield of 3.4 g. (34%) of the crude dimethylsulfonium dicyanomethylide hydrobromide was obtained.

A small portion of this hydrobromide was neutralized with sodium bicarbonate, as described above, to give a colorless solid, m.p. 98–99°, whose infrared spectrum was identical with that of an authentic sample of dimethylsulfonium dicyanomethylide. A mixture melting point of the two ylide samples showed no depression.

Diethylsulfonium Dicyanomethylide (Method C) (CTFEO).—To a solution of 23 g. (0.10 mole) of 2,2-dicyano-3,3-bis(trifluoromethyl)ethylene oxide (CTFEO) in 100 ml. of ether was added 18.0 g. (0.10 mole) of diethyl sulfide with stirring. After stirring at room temperature for 30 min., the white precipitate was isolated *via* filtration, washed with ether, recrystallized from ethanol, and dried. A total of 11.0 g. (74%) of diethylsulfonium dicyanomethylide, m.p. 85–86°, was obtained as colorless needles. The molecular weight (ebullioscopic in benzene) was found to be 154 (calcd., 154.2). The ultraviolet spectrum in ethanol showed λ_{max} 273 mμ (ε 5750).

Phenylmethylsulfonium Dicyanomethylide (Method C) (TCNEO).—A solution of 12.4 g. (0.10 mole) of thioanisole and 14.4 g. (0.10 mole) of tetracyanoethylene oxide (TCNEO) in a mixture of 25 ml. of tetrahydrofuran and 40 ml. of ether was allowed to stand at 22° for 24 hr. Volatile materials were removed under vacuum leaving a dark red oil. This oil was dissolved in ethylene chloride and chromatographed over 150 g. of basic alumina. After washing with 100 ml. of ethylene chloride to remove unreacted thioanisole, the column was washed with 600 ml. of acetonitrile. Removal of solvent from the eluate gave 12.9 g. (68%) of the impure ylide which was then recrystallized from methyl ethyl ketone to give colorless crystals, m.p. 77–78°.

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[12] All melting points are uncorrected.

Reactions of Amides and Sulfonamides with Nitrosonium Salts

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Amides and sulfonamides are converted to the corresponding acids by nitrosonium tetrafluoroborate (or related stable nitrosonium hexafluorophosphate, hexafluoroantimonate, hexafluoroarsenate, and bisulfate) at low temperatures and in organic solvent systems. Sterically hindered amides react generally with ease and good yields, although higher reaction temperatures are needed.

Amides which resist hydrolysis with alkalies or acids can be converted to the corresponding acids with a few exceptions by treating with nitrous acid.[2]

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2 + H_2O$$

Alkaline hydrolysis of hindered aromatic amides leads to the formation of nitriles. The acidic hydrolysis of hindered amides to acids by sulfuric acid–sodium nitrate treatment was investigated by Newman and co-workers.[3]

The reaction of amines with nitrosonium tetrafluoroborate was investigated previously.[4,5]

It was felt of interest to extend our investigations to the nitrosation of amides with nitrosonium tetrafluoroborate and related stable nitrosonium salts ($NO^+PF_6^-$, SbF_6^-, AsF_6^-, HSO_4^-). The reaction takes place generally at ice-bath temperature and leads to a quantitative formation of the corresponding acid.

$$RCONH_2 + NO^+BF_4^- \longrightarrow RCOOH + N_2 + HBF_4$$

The reaction with nitrosonium salts generally can be carried out in acetonitrile solution at ice-bath temperature and is quantitative. Sterically hindered amides need higher reaction temperatures. The aliphatic and aromatic amides, converted to their corresponding acids, are summarized in Table I.

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TABLE I

REACTION OF AMIDES WITH NITROSONIUM TETRAFLUOROBORATE

Amide	Acid	% yield
Acetamide	Acetic	71
Trifluoroacetamide	Trifluoroacetic	83
Trimethylacetamide	Pivalic	79
Diisopropylacetamide	Diisopropylacetic	69
Isobutylacetamide	Isobutylacetic	80
N-isopropylisopropyl-*t*-butylacetamide	Isopropyl-*t*-butylacetic	63
t-Butylethylacetamide	*t*-Butylethylacetic	70
Triphenylacetamide	Triphenylacetic acid	21
Tri-*n*-propylacetamide	Tri-*n*-propylacetic	61
Triisopropylacetamide	Triisopropylacetic	50
N-Isopropylisopropylacetamide	Isopropylacetic	73
n-Valeramide	*n*-Valeric	90
Benzamide	Benzoic	93
p-Toluamide	*p*-Toluic	95
o-Toluamide	*o*-Toluic	81
m-*t*-Butylbenzamide	*m*-*t*-Butylbenzoic	89
p-*t*-Butylbenzamide	*p*-*t*-Butylbenzoic	92
m-Ethylbenzamide	*m*-Ethylbenzoic	87
p-Ethylbenzamide	*p*-Ethylbenzoic	91
m-Isopropylbenzamide	*m*-Isopropylbenzoic	80
p-Isopropylbenzamide	*p*-Isopropylbenzoic	93
Mesitamide	Mesitoic	78
Duramide	Duroic	81
2,4,6-Triisopropylbenzamide	2,4,6-Triisopropylbenzoic	70

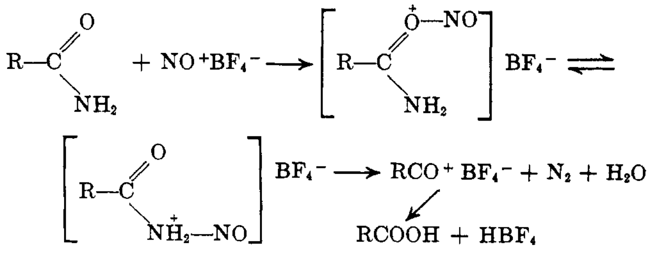
TABLE II

REACTION OF SULFONAMIDES WITH NITROSONIUM TETRAFLUOROBORATE

Sulfonamide	Sulfonic acid	% yield
Benzenesulfonamide	Benzenesulfonic	82
p-Toluenesulfonamide	*p*-Toluenesulfonic	87
2,4,6-Trimethylbenzenesulfonamide	2,4,6-Trimethylbenzenesulfonic	76

The solubility of the tetrafluoroborate and bisulfate salt is quite limited. Acetonitrile was found to be the only suitable solvent. The hexafluorophosphate and similarly hexafluoroantimonate and hexafluoroarsenate salts are more soluble, and with these salts nitromethane is a good solvent. Solutions of 10% or higher concentration can be obtained and removal of the solvent after completion of the reactions is easily achieved. Tetramethylene sulfone can also be applied as solvent, but its removal after reaction is more troublesome.

Although the hydrolysis of hindered amides (like triphenylacetamide) is much slower, the only exception to the reaction due to hindrance so far observed was that of *o*-*t*-butylbenzamide. This amide yielded with $NO^+BF_4^-$ *o*-*t*-butylbenzaldehyde and not *o*-*t*-butylbenzoic acid. Although some speculative mechanism could be offered to explain this unexpected reaction path, we at the present time have not enough experimental evidence to advance either of these. Concerning the mechanism of the reaction of amides with nitrosonium salts, it is proposed that the reactions proceed through primary O-nitrosation of the amides, followed by deaminative formation of an acylium ion which is unstable in the presence of equimolecular water formed in the reaction and gives the acid.



Protonation of amides is proven to involve the carbonyl oxygen and not the amide nitrogen atom, and an analogy in the primary interaction of amides with NO^+ is probable.

Sulfonamides react with nitrosonium tetrafluoroborate similarly to carboxylic acid amides (Table II).

$$RSO_2NH_2 + NO^+BF_4^- \longrightarrow RSO_3H + N_2 + HBF_4$$

Experimental

Amides used were either commercially available or samples were obtained through the generosity of Professor M. S. Newman, who described their preparation previously.[3]

Nitrosonium tetrafluoroborate was prepared as in previous work.[5] Samples of the salt as well as those of nitrosonium hexafluorophosphate, hexafluoroantimonate, and hexafluoroarsenate were also purchased from the Ozark-Mahoning Co., Tulsa, Okla. Nitrosonium bisulfate was obtained from the Allied Chemical Corp.

Reaction of Amides with Nitrosonium Salts. A. In Acetonitrile.—The amide (0.1 mole) was dissolved (suspended) in 150 ml. of acetonitrile. To the ice-cold and stirred solution 0.12 mole (17 g.) of nitrosonium tetrafluoroborate was added in 100 ml. of cold acetonitrile (the nitrosonium salt is only partially soluble and can be added as a slurry). Strong nitrogen evolution is observed. After the nitrogen evolution had subsided the now generally clear solution was briefly heated to 50°. After cooling, 5 ml. of water was added to destroy the excess nitrosonium salt. The solvent was pumped off *in vacuo*, and the residual acid was purified in the usual way (distillation and recrystallization). The amides that reacted and yields obtained are summarized in Table I. All the acids were known from the literature and were identified by their physical data (melting or boiling points) and infrared and n.m.r. spectra.

B. In Nitromethane.—A solution (or dispersion) of 0.1 mole of the amide was treated with a solution of 0.12 mole of nitrosonium hexafluorophosphate (antimonate or arsenate) with conditions similar to those under A.

Reaction of Sulfonamides with Nitrosonium Salts.—To a stirred and ice-cold solution of 0.1 mole of the sulfonamide in 50 ml. of acetonitrile was added a slurry of 0.1 mole of nitrosonium tetrafluoroborate in 60 ml. of acetonitrile. The reaction mixture was stirred until homogeneous solution was obtained and nitrogen evolution ceased. The solution was then briefly heated up to 50° to complete the reaction. The solvent was distilled *in vacuo*. The remaining sulfonic acids were purified by recrystallization.

Using nitrosonium hexafluorophosphate, the reactions could be carried out with nitromethane as solvent under conditions similar to those used in hydrolyzing amides.

Acknowledgment.—Professor M. S. Newman is thanked for his outstanding hospitality in the use of his laboratory and donation of samples of hindered amides.