N-Methyl-2-furimidoyl Chloride Hydrochloride (I). Hydrogen Chloride Procedure.—A solution of 2.5 g. (0.017 mole) of N-methyl-2-furimidoyl chloride in 40 ml. of petroleum ether was subjected to a stream of hydrogen chloride, diluted with nitrogen. The product, 2.6 g., was dried for analysis at 0.02 mm. for 2 hr.

With aniline I gave the corresponding **amidine**, which was identical by mixture melting point with the product obtained from N-methyl-2-furimidoyl chloride and aniline.

The other members (II–IX) were prepared in the same way, and the structures were verified by preparation of the amidines and determination of mixture melting points with the amidines prepared from the corresponding imidoyl chlorides (see Table I).

N-Methyl-2-furimidoyl Chloride Methochloride (X).—A mixture of 1.7 g. (0.012 mole) of N,N-dimethyl-2-furamide[25] and 4.0 g. (0.040 mole) of liquid phosgene in a sealed ampoule was treated as described in the general procedure. The product, 2.3 g., was a white crystalline powder. For analysis the compound was dried at 0.01 mm. for 4 hr.

N,N-Dimethyl-N′-phenyl-2-furamidine.—A suspension of X (1.6 g., 0.0084 mole) in 20 ml. of benzene was treated with a solution of 3.0 g. (0.0322 mole) of aniline in 10 ml. of benzene. The amidine (0.9 g., 52%) was a yellow viscous oil, b.p. 159–165° at 14 mm. The product was identified as its picrate, m.p. 122–123°. A mixture melting point with the picrate prepared from the methochloride, obtained by the phosphorus pentachloride procedure, was undepressed.

N,N-Dimethyl-N′-ethyl-2-furamidine was prepared from X and ethylamine, b.p. 95–99° at 12 mm.

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.48. Found: C, 65.12; H, 8.56.

A **picrate** was prepared from the amidine and picric acid. An analytical sample was obtained by recrystallization from aqueous ethanol, m.p. 106–109°.

Anal. Calcd. for $C_{15}H_{17}N_5O_8$: C, 45.57; H, 4.33; N, 17.72. Found: C, 45.83; H, 4.46; N, 17.83.

N-Ethyl-2-furimidoyl Chloride Ethochloride (XI).—A mixture of 1.3 g. (0.0078 mole) of N,N-diethyl-2-furamide[26] and 4.2 g. (0.043 mole) of liquid phosgene was treated as described in the general procedure. The product, 1.6 g., was a white crystalline solid. The sample was dried for analysis at 0.1 mm. for 4 hr.

N,N-Diethyl-N′-phenyl-2-furamidine.—A suspension of XI (2.5 g., 0.0113 mole) in benzene was treated with a solution of 4.2 g. (0.0451 mole) of aniline in 10 ml. of benzene. The amidine, 1.2 g. (44%), was a yellow viscous oil, b.p. 167–168° at 12 mm. The product was purified for analysis by fractional distillation.

Anal. Calcd. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49. Found: C, 74.25; H, 7.42.

The **picrate** was recrystallized from aqueous ethanol; m.p. 83–84°.

Anal. Calcd. for $C_{21}H_{21}N_5O_8$: C, 53.50; H, 4.49; N, 14.86. Found: C, 53.70; H, 4.60; N, 15.01.

N-Methylbenzimidoyl Chloride Methochloride (XII).[8,27]—A mixture of 1.2 g. (0.00804 mole) of N,N-dimethylbenzamide and 4.2 g. (0.043 mole) of liquid phosgene gave 1.6 g. of a white crystalline product, which was dried for analysis at 0.1 mm. for 7 hr. and melted in a sealed capillary tube under nitrogen at 124–125° (see Table I).

N,N-Dimethyl-N′-phenylbenzamidine was prepared from XII and aniline in a 64% yield. The picrate was purified from aqueous ethanol.

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S,S-Disubstituted Sulfonium Dicyanomethylides

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Synthesis and structure of stable sulfonium ylides containing the dicyanomethylide moiety is discussed. Three methods of preparation are presented along with the limitations of each. Physical properties of twelve sulfonium dicyanomethylides are listed. A brief study of the chemical properties of sulfonium dicyanomethylides has shown these compounds to be inert compared with previously known classes of sulfonium ylides. Specifically, they do not react with olefins or carbonyl reagents under conditions of the Wittig Reaction.

The class of compounds known as ylides encompasses zwitterions of the type ($^{+}YCR_2{}^{-}$) where Y is either R_3P–, R_3N–, R_3As–, or R_2S–. Generally speaking, these compounds are unstable and are usually proposed as intermediates in various rearrangement and elimination reactions.[2-6] In the course of work on cyano compounds, we became interested in sulfonium ylides which were substituted with cyano groups. Of the sulfonium ylides previously described in the literature, only those which bore an aromatic group on the α-carbon could be isolated, and even these were relatively unstable. These included the fluorenyl-,[7] substituted fluorenyl-,[8] and phenylsulfonium[9] ylides. Nonaromatic sulfonium ylides of the type prepared by Corey[4] were stable only in solution and at low temperatures. We wish to report now the synthesis of a new class of ylides, the sulfonium dicyanomethylides, which are unique in their chemical and thermal stability.

This new class of sulfonium ylide can be represented by the following structures. The simplest member of the class, the dimethyl derivative was first prepared by the condensation of dimethyl sulfoxide with malononitrile in the presence of hydrogen chloride or thionyl chloride. The resulting dihydrochloride was then neutralized with base to give the free ylide in 41% yield

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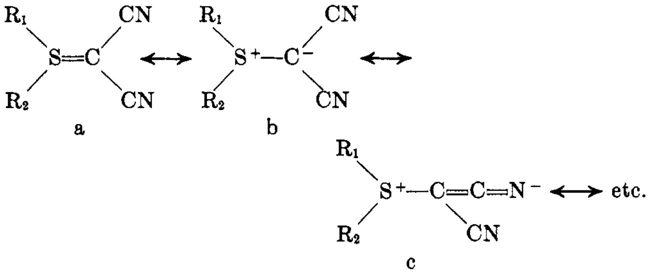
Table I

S,S-Disubstituted Dicyanomethylides

R_1	R_2	Moment (D)	Yield,[a] %	M.p., °C.[b]	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
CH_3	CH_3		77	100–101	$C_5H_6N_2S$	47.59	47.74	4.79	4.83	22.21	22.35
C_2H_5	C_2H_5		74[c]	85–86	$C_7H_{10}N_2S$	54.52	54.79	6.54	6.28	18.17	18.16
C_4H_9	C_4H_9	7.7	62	29–30	$C_{11}H_{18}N_2S$	62.89	62.98	8.58	8.76	13.33	13.31
$(CH_2)_4$			80,[c] 42	94–95	$C_7H_8N_2S$	55.23	55.60	5.30	5.67	18.41	18.13
CH_3	$C_{12}H_{25}$		85, 57[c]	46–47	$C_{16}H_{28}N_2S$	68.59	68.25	10.00	9.92	10.00	9.81
CH_3	C_6H_5		68, 70[c]	77–78	$C_{10}H_8N_2S$	63.90	64.02	4.25	4.42	14.88	14.64
C_2H_5	C_6H_5	7.6	75	75–76	$C_{11}H_{10}N_2S$	65.34	65.10	5.00	5.14	13.88	14.14
C_4H_9	C_6H_5		74	Oil	$C_{13}H_{14}N_2S$	67.82	67.29	6.09	6.26	12.17	. . .
CH_3	$C_{10}H_7$	8.1	74	136–137	$C_{14}H_{10}N_2S$	70.62	70.78	4.21	4.44	11.75	11.67
CH_3	p-$CH_3OC_6H_4$	8.0	67	92–93	$C_{11}H_{10}N_2OS$	60.60	60.76	4.59	4.55	12.84	13.02
CH_3	p-BrC_6H_4	7.0	45	124–125	$C_{10}H_7BrN_2S$[d]	44.96	. . .	2.62	. .	10.49	10.53
CH_3	p-$CH_3SC_6H_4$		26[c]	136–137	$C_{11}H_{10}N_2S_2$[e]	56.42	55.92	4.27	4.44	11.97	11.58

[a] Yields are based on method C. [b] All melting points are uncorrected. [c] Prepared from CTFEO; all others from TCNEO. [d] Bromine: calcd., 29.94; found, 30.14. [e] Sulfur: calcd., 27.34; found, 27.40.



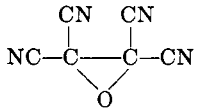
(method A). In an alternative procedure, dehydro-

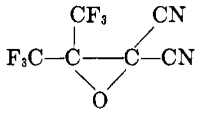
$$(CH_3)_2SO + CH_2(CN)_2 \xrightarrow{SOCl_2} (CH_3)_2S^+{-}C^-(CN)_2 \cdot 2HCl \xrightarrow{B^-} \underset{\text{I}}{(CH_3)_2S^+{-}C^-(CN)_2}$$

bromination of the dimethyl sulfide bromomalonitrile adduct also gave I in 20% yield (method B). For an

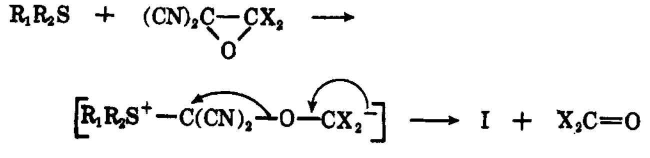
$$(CH_3)_2S + CHBr(CN)_2 \longrightarrow (CH_3)_2S^+{-}CH(CN)_2Br^- \xrightarrow{B^-} \text{I}$$

as yet unexplained reason, methods A and B are specific for the dimethyl compound (I) and higher homologs could not be prepared *via* these synthetic routes. A more general route to sulfonium dicyanomethylides was found, however, by utilizing either tetracyanoethylene oxide (TCNEO)[10] or 2,2-dicyano-3,3-bis(trifluoromethyl)ethylene oxide (CTFEO)[11] in reaction with


TCNEO


CTFEO

various sulfides (method C). Method C has been used to prepare a variety of dialkyl- and aralkylsulfonium dicyanomethylides which are listed in Table I. In at least one case (diphenyl sulfide), diaryl derivatives could not be prepared using this method.

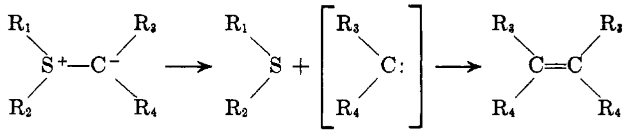


X = CN for TCNEO; CF_3 for CTFEO

The most interesting feature of these compounds is their stability relative to other sulfonium ylides. The dicyanomethylides are generally crystalline solids, which melt sharply without decomposition, but which discolor upon prolonged heating of the melt (2–5 hr.). They do not undergo reactions with aldehydes or olefins, are stable to hydrogen peroxide oxidation, and are unaffected by moisture, alcohols, and weak acids or bases. Cold mineral acid cleaves the ylide into the original sulfide plus other unidentified products. This chemical stability is probably due to the stabilizing effect of the two cyano groups. Structure a has been credited[3] with imparting stability to sulfur and phosphorus ylides by virtue of the overlap of the free electron pair with the vacant d-orbitals of the hetero atoms. In the dicyanomethylides, however, additional stability can be rationalized by structures such as c. The infrared absorption spectra of the ylides show bands at 4.58–4.60 and 4.64–4.66 μ, indicating an appreciable amount of ionic character for the cyano groups and thus supporting c as an important contributor to the over-all electronic structure. The delocalization of the negative charge over the two cyano groups must greatly reduce any nucleophilic reactivity of the molecule. Since classical ylide reactions are postulated as proceeding by an initial nucleophilic attack by the ylide α-carbon atom on an electron-deficient carbon atom (carbonyl carbon), any stabilizing groups would cause a pronounced decrease in ylide reactivity.

By way of comparison we can look at the dimethylsulfonium fluorenylides.[8] Introduction of electron-withdrawing groups on the fluorenyl moiety leads to increased stability and decreased reactivity. The unsubstituted ylide is isolable only at low temperatures and is rapidly degraded; 2-nitrofluorenylide is stable at room temperature for several days and the 2,7-dinitrofluorenylide is stable indefinitely.

Although the sulfonium dicyanomethylides do not undergo any of the reactions common to the more reactive sulfonium ylides, their thermal degradation is somewhat similiar. Hughes and Kuriyan[8] demonstrated that thermal degradation of the dimethyl-



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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°.

(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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