Iminosulfuranes. XI.[1] Preparation, Properties, Mass Spectral Fragmentation, and Thermolysis of *N*-Ethoxycarbonyliminodialkylsulfuranes

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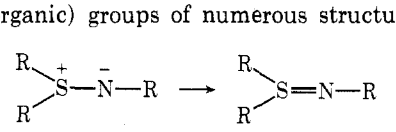
N-Ethoxycarbonyliminodialkylsulfuranes, a new class of iminosulfuranes, are obtained in good yield by the reaction of *N*-monochlorourethane with dimethyl and diethyl sulfides, followed by treatment of the intermediate sulfonium salts with triethylamine. Mass spectral fragmentation and thermolysis of the ylides and their precursor salts have been studied and some similarities have been observed in the decomposition pathways. Spectral and reactivity information indicate that the iminosulfuranes exist largely as charge-delocalized species. They are unreactive toward the electrophiles acrylonitrile, ethyl acrylate, *p*-nitrobenzaldehyde, and styrene oxide. An iminophosphorane, *N*-ethoxycarbonyliminotriphenylphosphorane, structurally related to the iminosulfuranes reported, was also prepared; it too was unreactive toward benzaldehyde and styrene oxide.

Iminosulfuranes[3] are resonance hybrids of the general structure 1 in which the R groups are organic (and occasionally inorganic) groups of numerous structural types.[4]



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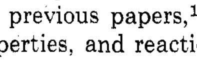
The best known 1 are *N*-sulfonyliminosulfuranes (2), and a vast body of literature exists on their preparation, properties, and reactions. They are the first types of 1 reported[5-7] and they appear to be the most stable. The strongly electron-withdrawing sulfonyl group attached to nitrogen effectively delocalizes its negative charge, thus resulting in enhanced stability of 2 toward hydrolysis, and permits laboratory manipulation and storage without special precautions. In contrast, when the group attached to nitrogen is electron donating or hydrogen (3), the compounds are extremely reactive, moisture sensitive, and difficult to store and handle; it is not absolutely certain whether examples of analytically pure 3 have yet been prepared owing to their lability.[8-10]



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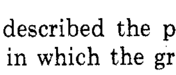


3

In two previous papers,[11,12] we described the preparation, properties, and reactions of 1 in which the group attached to nitrogen is acyl (moderately electron withdrawing). These iminosulfuranes can be readily obtained in good yields from dialkyl sulfides and *N*-halo amides in mixed solvents at moderate temperatures (0°) without special precautions. In this paper we describe the preparation, properties, and thermolysis reactions of a new class of iminosulfuranes, *N*-ethoxycarbonyliminodialkylsulfuranes (5), and their precursor sulfonium chlorides (4) from dialkyl sulfides and ethyl *N*-chlorocarbamate (*N*-monochlorourethane, 6) (eq 1). Ir, nmr, uv, mass spectrometry, and elemental analysis were used to substantiate the structures of 4 and 5 and their thermolysis products.

$$R_2S + \underset{6}{ClNHCO_2C_2H_5} \xrightarrow[0\ \text{to}\ -20°]{CHCl_3\ \text{or}\ CCl_4}$$

$$R = CH_3, C_2H_5$$

$$\underset{4}{[R_2\overset{+}{S}{-}NHCO_2C_2H_5]Cl^-} \xrightarrow[0°]{(C_2H_5)_3N} \underset{5}{R_2\overset{+}{S}{-}\overset{-}{N}CO_2C_2H_5} \quad (1)$$

Results and Discussion

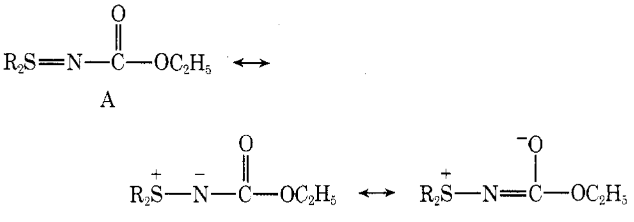
Preparation of Ylide Salts and Ylides. Reaction of ethyl *N*-chlorocarbamate (6) with dimethyl sulfide in dry chloroform at 0–5° affords a 55% yield of analytically pure *N*-ethoxycarbonyliminodimethylsulfonium chloride (8), a white, crystalline, hygroscopic solid, stable at room temperature but decomposing at its melting point, 121.5°. (The salt must be thoroughly dry to obtain the reported melting point.)

The homologous *N*-ethoxycarbonyliminodiethylsulfonium chloride (10) is obtained in 60% yield from diethyl sulfide and 6 at −15 to −20° in dry carbon tetrachloride. The salt is also a crystalline, hygroscopic solid that decomposes rapidly at its melting point, 98–99°, and slowly in chloroform at room temperature. We have had occasional difficulties in preparing 10 in chloroform at low temperatures and no success with hexane or benzene as reaction solvents. The successful preparation of 10 in carbon tetrachloride is attributed to the insolubility of the salt, resulting in precipitation as it forms. 10 is stable in water and dimethyl sulfoxide solutions.

Diisopropyl, di-*tert*-butyl, and diphenyl sulfides do not form sulfonium salts under similar reaction conditions. We do not understand why diisopropyl sulfide fails to react normally with 6, as it reacts readily with *N*-halo amides.[11] It is assumed that di-*tert*-butyl sulfide fails to react as anticipated for steric reasons. In diphenyl sulfide the lone-pair electrons on sulfur are presumably so well delocalized into the aromatic rings that they are unavailable for displacement of halogen from 6. The only products obtained from the reaction of 6 with diphenyl sulfide are ethyl carbamate and diphenyl sulfoxide; from diisopropyl and di-*tert*-butyl sulfides only ethyl carbamate (99–100%) is isolated.

Treatment of 8 and 10 with a small excess of triethylamine in chloroform or methylene chloride, respectively, at 0–5° furnishes the corresponding pure iminosulfuranes, *N*-ethoxycarbonyliminodimethylsulfurane (9) and *N*-ethoxycarbonyliminodiethylsulfurane (11), as colorless (or slightly yellow), viscous liquids in 85–90% yields. They are considerably more stable than their precursor salts and can be distilled in a Kugelrohr apparatus below 150° without decomposition, although distillation is unnecessary if one uses pure salts in the ylide preparations. Particular caution must be exercised in distilling 11, as it readily decomposes at or above 150° to ethylene and ethyl *N*-(ethylthio)carbamate (see later discussion).

Spectra of Ylide Salts and Ylides. Ir spectra of 8 and 10 (KBr disks) show bands in the secondary amine region at 3420–3465 (m–w) and carbonyl (s) at 1735–1740 cm^{-1}. In contrast, the ir spectra of neat 9 and 11 show no bands at 3420-3465 cm^{-1} and the carbonyl absorptions shift to 1620-1630 cm^{-1}, a frequency reduction of over 100 cm^{-1}. The shift of the carbonyl absorption is analogous to that observed in converting carboxylic acids to carboxylate ions and suggests that the iminosulfuranes have the ionic structure C shown below rather than the double-bond structure A. The uv spectra of **9** and **11**, however, show a maximum at about 219 nm with ϵ_{max} of about 2200-2350 (Beer-Lambert law not followed), indicating that structure A must also be making a contribution. The low value of ϵ_{max} suggests that structure A, involving 3d-2p overlap between sulfur and nitrogen, is a minor contributor; the large reduction in the carbonyl frequency from ylide salt to ylide suggests that C is a major contributor.



$$R_2S{=}N{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 \longleftrightarrow$$

A

$$R_2\overset{+}{S}{-}\overset{-}{N}{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 \longleftrightarrow R_2\overset{+}{S}{-}N{=}\overset{^{-}O}{\overset{|}{C}}{-}OC_2H_5$$

B C

Structure B must also be a significant canonical form, as shown by comparing the nmr spectra of the salts (**8**, **10**) with those of the ylides (**9**, **11**). A noteworthy feature of the nmr spectra is the substantial upfield shift (0.6 and 1.2 ppm, respectively) in the signals of the methyl [$-S(CH_3)_2^+$] and methylene [$-S(\mathbf{CH_2}CH_3)_2^+$] protons attached to sulfur in the ylides. In the ylides, the positive charge on sulfur must be partially neutralized by the negative charge on nitrogen (B), thus resulting in less deshielding (upfield signals), whereas in the salts there is a full formal positive charge on sulfur which exerts a larger deshielding effect (downfield signals). The same conclusion would be reached if A were a major canonical form, but the low value of ϵ_{max} argues against such a proposal.

Thermolysis of *N*-Ethoxycarbonyliminodimethylsulfonium Chloride (8). Heating salt **8** under nitrogen first to 100-155° until gas evolution ceases and then to 160° to remove volatile species yields three major products and a minor one: bis(methylthio)methane (**12**), 1,1-bis(*N*-ethoxycarbonylimino)methane (**13**), hydrogen chloride, and ethyl carbamate (**7**) (yields are based on the assumed stoichiometry shown). The products were identified by spectral and analytical measurements and, where necessary (**12** and **13**), by comparison with authentic samples. In control experiments, products **12** and **13** were shown to be stable under the thermolysis conditions.

$$\underset{\mathbf{8}}{2[(CH_3)_2\overset{+}{S}{-}NHCO_2C_2H_5]Cl^-} \xrightarrow[\text{2. }160°]{\text{1. }100\text{-}115°}$$

$$\underset{\mathbf{12}(50\%)}{(CH_3S)_2CH_2} + \underset{\mathbf{13}(25-50\%)}{CH_2(NHCO_2C_2H_5)_2} + \underset{20-35\%}{2HCl} + \underset{\mathbf{7}(1-5\%)}{H_2NCO_2C_2H_5}$$

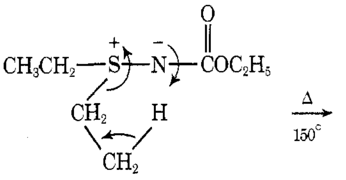
Thermolysis of *N*-Ethoxycarbonyliminodiethylsulfonium Chloride (10). Thermolysis of **10** at 95-100° under nitrogen until gas evolution ceases yields three major products and a minor one: diethyl sulfide, ethyl carbamate (**7**), hydrogen chloride, and 1,1,2,2-tetrakis(*N*-ethoxycarbonylimino)ethane (**14**)[19] (yields are based on the assumed stoichiometry shown). Thermolysis of **10** must follow a totally different pathway from that of **8** because the product types and their distribution are significantly different. The initial step cannot be formation of ylide **11**, as thermolysis of that compound (see below) follows a different decomposition pathway from that of salt. Although multistep pathways can be written to rationalize the thermolysis of **10**, especially for the formation of **14**, no evidence or precedents appear to be available; therefore, no speculations will be offered until further experimental data are collected.

$$\underset{\mathbf{10}}{[(C_2H_5)_2\overset{+}{S}{-}NHCO_2C_2H_5]Cl^-} \xrightarrow{95\text{-}100°}$$

$$\underset{40\%}{(C_2H_5)_2S} + \underset{\mathbf{7}(50\%)}{NH_2CO_2C_2H_5} + \underset{30\%}{HCl} + \underset{\mathbf{14}(8\%)}{(C_2H_5OCONH)_2CHCH(NHCO_2C_2H_5)_2}$$

In chloroform solution at room temperature for 48 hr, **10** decomposes to a mixture of products of which ethyl carbamate is the major one (75%).

Thermolysis of *N*-Ethoxycarbonyliminodiethylsulfurane (11). Thermolysis of **11** at 150° until gas evolution ceases yields ethylene and ethyl *N*-(ethylthio)carbamate (**15**) as the major products; ethyl carbamate, 1,1-bis(*N*-ethoxycarbonylimino)ethane,[22,23] and various unidentified compounds are minor products. The thermolytic decomposition of **11** exactly parallels that observed with *N*-acetyliminodialkylsulfuranes previously reported by us.[12] The key structural requirement in the ylide is the presence of at least one β-hydrogen atom in the alkyl group attached to sulfur. A five-center cyclic concerted mechanism readily accounts for the formation of alkene and **15**. In the thermolysis of *N*-*p*-toluenesulfonyliminoethylphenylsulfurane, Oae and coworkers[24] have reported a similar decomposition. They showed that the reaction is first order in ylide and a substantial kinetic isotope effect k_H/k_D is observed, consistent with the proposed mechanism. The thermolysis of ylides, such as **11**, is a convenient way to prepare *N*-alkylthiocarbamates.



11

$$\xrightarrow[150°]{\Delta}$$

$$\underset{8-35\%}{CH_2{=}CH_2} + \underset{\mathbf{15}\,(45-60\%)}{CH_3CH_2SNHCO_2C_2H_5} + \underset{15\%}{NH_2CO_2C_2H_5} + \underset{5\%}{CH_3CH(NHCO_2C_2H_5)_2}$$

Mass Spectral Fragmentation of 8 and 9. The mass spectral fragmentation patterns of ylide salt **8** and ylide **9** are very similar; they are summarized in a superimposed, condensed form in Scheme I. The primary fragmentation of ylide salt **8** is loss of HCl to yield iminosulfurane **9**. A subsequent prototropic shift yields the sulfurane, which loses methylene to yield ethyl *N*-(methylthio)carbamate, *m/e* 135, or undergoes a Stevens-type rearrangement to ethyl *N*-(methylthiomethyl)carbamate, *m/e* 149. No peaks due to 1,1-bis(*N*-ethoxycarbonylimino)methane (**13**) or bis(methylthio)methane (**12**) are observed either from salt or ylide (contrast with thermolysis of **8** discussed earlier).

Loss of methylene is an unusual process in mass spectrometry and the ease with which it occurs in this case is strong evidence that the iminosulfurane rearranges prototropically to the sulfurane (Scheme I). An analogous 1,3-prototropic shift and subsequent loss of methylene has been reported by Robson, Speakman, and Stewart,[25] who found that the high-resolution mass spectrum of dimethylsulfonium 1-dodecylsulfonylmethylide (**17**) shows a mo-

EXPERIMENTAL SECTION

The physical data were obtained as follows: melting points (uncorrected) with a Thomas-Hoover melting point apparatus; ir spectra with a Perkin Elmer 225 or 137B; uv spectra with a Perkin Elmer 202; nmr spectra with a Varian A-60A or, occasionally, XL-100-15 using tetramethylsilane as internal standard (δ = 0.00); mass spectra with an A.E.I. MS-9 double focusing mass spectrometer by direct insertion at 70 ev (Battelle Memorial Institute, Columbus, Ohio). Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Delaware. Tlc and glc assessments of purity were conducted with appropriately designed systems and operating conditions as described under the specific cases. All solvents were dried and freshly distilled before use.[13]

Ethyl-N-chlorocarbamate [N-Monochlorourethane (6). Prepared in approximately 50% yield by passing gaseous chlorine through a vigorously stirred 20% aqueous solution of ethyl carbamate (urethane) (7) at 0-5° (molar ratio 6:Cl_2, 1:1) followed by vacuum distillation at low temperature; bp 44-45° (0.2 torr).[14] A superior procedure, developed toward the end of this study, is the disproportionation reaction between 7 and ethyl N,N-dichlorocarbamate (N,N-dichlorourethane) at room temperature in the dark; yields of 6 are essentially quantitative without distillation.[15]

N-Ethoxycarbonyliminodimethylsulfonium Chloride (8). A solution of 6 (13.4 g, 0.11 mol, 92% pure by iodometry) in dry chloroform (15 ml) was added dropwise with stirring to a solution of dimethyl sulfide (7.5 g, 0.12 mol, 100% pure by glc) in dry chloroform (200 ml) at 2-4° over 70 min. Reaction was continued for an additional 35 min at 1-2° and the volatiles were then removed using a rotary evaporator (water bath at 28°). Ether (200 ml) was added to the residue and the mixture was agitated for 30 min on a mechanical shaker. The white solid residue was collected by filtration and dried to constant weight in a vacuum desiccator at room temperature to give the crude salt (8) (14.9 g, 74%, mp 114.5° dec). A portion (1.5 g) of the crude product was dissolved in methanol-ether (150 ml, 1:4) at room temperature and left at 0° for 2 days. The white crystalline solid was filtered and dried under vacuum at room temperature to give pure 8 (1.1 g, mp 121.5° dec, 55%). The salt (8) is hygroscopic and must be thoroughly dry to obtain the reported mp. Drying should be conducted at room temperature or below to avoid thermolytic decomposition.

Ir (KBr disc) 3465 (w) (N-H stretch), 1740 (s) (C=O stretch), 1445 (s), 1220 (s) (C-O stretch), 991 (s), 839, 754 cm^{-1} (m) (S-N stretch); nmr (DMSO-d_6) δ 8.10 (concentration dependent) (s, 1, N$\underline{H}$), 4.23 (q, 2, J = 7 cps, $CH_3C\underline{H}_2O$), 3.37 (s, 6, $(C\underline{H}_3)_2\overset{+}{S}$), 1.27 (t, 3, J = 7 cps, $C\underline{H}_3CH_2O$).

Anal. calcd. for $C_5H_{12}ClNO_2S$ (8): C, 32.34; H, 6.51; Cl, 19.10; N, 7.54; S, 17.27. Found: C, 32.12; H, 6.26; Cl, 19.31; N, 7.52; S, 17.08.

Mass Spectrum (8) (direct insertion at 100°):[16] m/e 149, (9), M-HCl, $C_5H_{11}NO_2S$ (6.9 ppm); 135, (2), M-(HCl + :CH_2), $C_4H_9NO_2S$ (4.6 ppm); 134, (1), M-(HCl + CH_3), $C_4H_8NO_2S$ (6.4 ppm); 121, (3), m/e 149 - C_2H_4, $C_3H_7NO_2S$ (9.7 ppm); 104, (100), m/e 149-OEt, C_3H_6NOS (3.2 ppm); 102, (1), m/e 149 - CH_3S, $C_4H_9NO_2$ (6.1 ppm); 90, (1), m/e 104-:CH_2, C_2H_4NOS (8.3 ppm); 89, (9), m/e 135 - EtOH, C_2H_3NOS (0.8 ppm); 74 (2), m/e 121 - CH_3S, $C_2H_4NO_2$ (5.1 ppm); 63, (3) m/e 135 - (CO_2 + C_2H_4), CH_5NS (38.3 ppm); 62, (72), m/e 104 - NCO, C_2H_6S (38.4 ppm); 62, (13), m/e 135 - CO_2Et, CH_4NS (46.7 ppm); 47, (16), CH_3S (10.3 ppm); 45, (8), CHS (19.1 ppm); 38, (15), $H^{37}Cl$ (22.6 ppm); 36 (48), $H^{35}Cl$ (29.9 ppm); 30, (4), CH_4N (3.6 ppm); 29, (18), C_2H_5 (9.8 ppm).

N-Ethoxycarbonyliminodimethylsulfurane (9). A solution of dry redistilled triethylamine (7.1 g, 0.071 mol) in dry chloroform was added dropwise with stirring to a suspension of 8 (10.9 g, 0.059 mol) in dry chloroform (250 ml) at 0-5° over 60 min, and stirring was continued for an additional 10 min. The volatiles were removed using a rotary evaporator (water bath at 40°) and ether (100 ml) was added to the residue. The precipitated triethylamine hydrochloride (8.2 g, 100%) was separated by filtration and the filtrate was evaporated. A pale yellow oil was obtained which was dried to constant weight at room temperature under vacuum; tlc analysis showed only one spot, R_F 0.70 (silica gel 0.25 mm, developed with methanol and detected with iodine vapor). It was shown to be analytically pure 9 without further treatment (7.7 g, 88%, n_D^{25} 1.4995).

Ir (liquid film) 1620 (s) (C=C stretch), 1275 (s) (C-O stretch), 1097 (s), 980 (m), 821, 782 cm^{-1} (m) (S-N stretch); uv (C_2H_5OH) λ_{max} 219 nm, ε_{max} 2200 (5.25 x 10^{-4} mol/l) (the absorption did not follow the Beer-Lambert law over the concentration range 1.05-10.5 x 10^{-4} mol/l); nmr ($CDCl_3$) δ 4.06 (q, 2, J = 7 cps, $CH_3C\underline{H}_2O$), 2.71 (s, 6 $(C\underline{H}_3)_2\overset{+}{S}$), 1.24 (t, 3, J = 7 cps, $C\underline{H}_3CH_2O$).

Anal. calcd. for $C_5H_{11}NO_2S$ (9): C, 40.25; H, 7.43; N, 9.39; S, 21.44. Found: C, 40.00; H, 7.27; N, 9.11; S, 21.49.

Mass Spectrum (9)(direct insertion at 100°): m/e 149, (10), molecular ion, $C_5H_{11}NO_2S$ (5.3 ppm); 135, (2), M- :CH_2, $C_4H_9NO_2S$ (7.1 ppm); 121, (2), m/e 149 - C_2H_4, $C_3H_7NO_2S$ (0.7 ppm); 104, (100), m/e 149 - OEt, C_3H_6NOS (15.6 ppm); 102, (2), m/e 149 - CH_3S; 89, (7), m/e 135 - EtOH, C_2H_3NOS (2.2 ppm); 74, (2), m/e 121 - CH_3S, $C_2H_4NO_2$ (6.3 ppm); 63, (2), m/e 135 - (CO_2 + C_2H_4), CH_5NS (24.0 ppm); 62, (80), m/e 104 - NCO, C_2H_6S (13.5 ppm); 62, (14), m/e 135 - CO_2Et, CH_4NS (19.0 ppm); 47, (18), CH_3S (11.6 ppm); 45, (11), CHS (3.7 ppm); 30, (5), CH_4N (5.7 ppm); 29, (21), C_2H_5 (14.8 ppm).

N-Ethoxycarbonyliminodiethylsulfonium Chloride (10). A solution of 6 (12.35 g, 0.10 mol, 99.5% pure by iodometry) in redistilled carbon tetrachloride (40 ml) was added dropwise with stirring to a solution of diethyl sulfide (10.8 g, 0.12 mol) in redistilled carbon tetrachloride (240 ml) at -15 to -20° over 65 min. The reaction was slightly exothermic and a precipitate began to appear after about 50 min from the start of the reaction. The reaction mixture was stirred at -15 to -20° for an additional 30 min after the addition of 6 was complete and the white precipitate (10) was then filtered off and dried under vacuum to constant weight at 20-25° (14.5 g). The crude salt (10) was shaken vigorously for 30 min with redistilled carbon tetrachloride in a mechanical shaker and filtered. After drying to constant weight under vacuum at 20-25°, pure 10 was obtained (13.1 g, 61%, mp 98-99° dec). Salt 10 is hygroscopic.

Ir (KBr disc) 3420 (m) (N-H stretch), 1735 (s) (C=O stretch), 1440 (m), 1216 (s) (C-O stretch), 839, 762 cm^{-1} (w) (S-N stretch); nmr ($CDCl_3$) δ 4.34 (q, 2, J = 7 cps, $CH_3C\underline{H}_2O$), 4.15, 4.10 [two quartets, 4, J = 7 cps, $(CH_3C\underline{H}_2)_2\overset{+}{S}$], 2.70 (concentration dependent) (broad s, 1, N$\underline{H}$), 1.55 (t, 6, J = 7 cps, $[(C\underline{H}_3CH_2)_2\overset{+}{S}]$, 1.33 (t, 3, J = 7 cps, $C\underline{H}_3CH_2O$). At 60 MHz, the signal due to $(CH_3C\underline{H}_2)_2\overset{+}{S}$ appeared to be two overlapping quartets but at 100 MHz in DMSO-d_6, the signal consisted of 14 lines symmetrical about δ 3.81.

Anal. calcd. for $C_7H_{16}ClNO_2S$ (10): C, 39.33; H, 7.55; Cl, 16.59; N, 6.55; S, 15.00. Found: C, 39.55; H, 7.44; Cl, 16.34; N, 6.38; S, 15.31.

Mass Spectrum (10)(direct insertion at 60°): m/e 177, (6), M-HCl, $C_7H_{15}NO_2S$ (0.3 ppm); 149, (24), m/e 177 - C_2H_4, $C_5H_{11}NO_2S$ (1.2 ppm); 148, (1), m/e 177 - C_2H_5, $C_5H_{10}NO_2S$ (8.7 ppm); 132, (40), m/e 177 - OEt, $C_5H_{10}NOS$ (4.8 ppm); 116, (4), m/e 177 - EtS, $C_5H_{10}NO_2$ (7.1 ppm); 104, (12), m/e 132 - C_2H_4, C_3H_6NOS (10.7 ppm); 103, (7), m/e 149 - EtOH, C_3H_5NOS (0.6 ppm); 90, (100), m/e 149 - C_2H_3S, $C_3H_8NO_2$ (9.7 ppm); 77, (20), m/e 149 - (CO_2 + C_2H_4), C_2H_7NS (0.1 ppm); 76, (20), m/e 104 - CO, C_2H_6NS (2.6 ppm); 62, (16), m/e 90 - C_2H_4, CH_4NO_2 (15.8ppm); 62, (22), m/e 77 - CH_3, CH_4NS (8.7 ppm); 61, (42), m/e 104 - HNCO, C_2H_5S (13.6 ppm); 60, (17), m/e 77 - NH_3, C_2H_4S (15.7 ppm); 59, (12), m/e 76 - NH_3, C_2H_3S (15.8 ppm); 49 (34), m/e 77 - C_2H_4 , H_3NS (0.3 ppm); 48, (24), m/e 76 - C_2H_4, H_2NS (4.4 ppm); 38, (17), $H^{37}Cl$ (25.0 ppm); 36, (51), $H^{35}Cl$ (29.4 ppm); 29, (80), C_2H_5, (5.5 ppm); 28, (40), C_2H_4 (16.1 ppm).

N-Ethoxycarbonyliminodiethylsulfurane (11). Dry redistilled triethylamine (1.14 g, 0.011 mol) was added dropwise with stirring to a solution of 10 (2.0 g, 0.009 mol) in dry methylene chloride (9 ml) at 0-4° over 60 min. When addition was complete, ether (35 ml) was added and the precipitate of triethylamine hydrochloride (1.27 g, 98%, mp 257-259°) was filtered. The filtrate was evaporated in a rotary evaporator (water bath 27°) to give a pale yellow liquid (1.7 g, 100%) which could be distilled in a Kugelrohr apparatus below 150° *without any apparent decomposition. The product [1.49 g, 95%, bp 135-149°* (0.05 torr)] was a colorless liquid; tlc analysis showed one major spot, R_F 0.84 and one extremely faint spot, R_F 0.58 (silica gel 0.25 mm, developed with acetone and detected with iodine vapor). Distillation is not required for purification, but merely improves the color; if the distillation temperature is not properly controlled thermolytic decomposition occurs (see below).

Ir (liquid film) 1630 (s) (C=O stretch), 1260 (s) (C-O stretch), 1097 (m), 826, 782 cm^{-1} (m) (S-N stretch); uv (C_2H_5OH) λ_{max} 219.5 nm, ε_{max} 2350 (4.86 x 10^{-4} mol/l) (the absorption did not follow the Beer-Lambert law over the concentration range 2-6 x 10^{-4} mol/l); nmr ($CDCl_3$) 4.06 (q, J = 7 cps, $CH_3C\underline{H}_2O$), 2.93 (q, 4, J = 8 cps, $(CH_3C\underline{H}_2)_2\overset{+}{S}$), 1.35 (t, 6, J = 8 cps, $(C\underline{H}_3CH_2)_2\overset{+}{S}$), 1.24 (t, 3, J = 7 cps, $C\underline{H}_3CH_2O$).

Anal. calcd. for $C_7H_{15}NO_2S$ (11): C, 47.42; H, 8.53; N, 7.90; O, 18.05; S, 18.09. Found: C, 47.12; H, 8.57; N 8.08; O, 18.17; S, 18.23.

Mass spectrum (11) (direct insertion at 100°): m/e 177, (13), molecular ion $C_7H_{15}NO_2S$ (0 ppm); 149, (13), M-C_2H_4, $C_5H_{11}NO_2S$ (5.4 ppm); 148, (4), M-Et, $C_5H_{10}NO_2S$ (8.6 ppm); 132, (85), M-OEt, $C_5H_{10}NOS$ (0 ppm); 121, (2), m/e 149 - C_2H_4, $C_3H_7NO_2S$ (14.9 ppm); 116, (1.5) M-EtS, $C_5H_{10}NO_2$ (11.7 ppm); 104, (24), M-(OEt + C_2H_4), C_3H_6NOS (5.9 ppm); 90, (92), m/e 149 - C_2H_3S, $C_3H_8NO_2$ (15.7 ppm); 77, (13), m/e 149 - (C_2H_4 + CO_2), C_2H_7NS (11.4 ppm); 76, (14), m/e 149 - CO_2Et and m/e 104 - CO, C_2H_6NS (9.1 ppm); 75, (6), m/e 121 - EtOH, CHNOS (3.6 ppm); 62, (15), m/e 90-C_2H_4, CH_4NO_2 (29.3 ppm); 61, (62), m/e 104 - HNCO, C_2H_5S (9.4 ppm); 59, (10), C_2H_3S (27.4 ppm); 49, (18), m/e 77 - C_2H_4 and m/e 121 - (CO + C_2H_4), H_3NS (7.2 ppm); 48, (19), m/e 121 - CO_2Et and m/e 76 - C_2H_4, H_2NS (2.6 ppm); 29, (50), C_2H_5 (4.3 ppm); 28, (25), C_2H_4 (19.2 ppm); 18, (100), H_2O (0 ppm).

Reaction of Ethyl N-Chlorocarbamate (6) with Other Sulfides. A solution of 6 (6.2 g, 0.05 mol) in dry chloroform (25 ml) was added with stirring to a solution of di-*t*-butyl sulfide (11 g, 0.075 mol) in chloroform (75 ml) at 0° over 100 min (exothermic reaction). Evaporation of volatiles in a rotary evaporator yielded a white solid residue that was recrystallized from *n*-hexane-ether; it was identified by mp and nmr as ethyl carbamate (4.4 g, 99%).

Analogous reaction of 6 with diisopropyl sulfide in carbon tetrachloride at -15° yielded only ethyl carbamate (4.5 g, 100%) as an insoluble precipitate formed during the reaction. Diphenyl sulfide also failed to yield the expected sulfonium salt; ethyl carbamate and some diphenyl sulfoxide were formed but most of the diphenyl sulfide was recovered unchanged.

Thermolysis of 8. A sample of 8 (5.22 g, 0.0282 mol) was placed in a flask fitted with a nitrogen gas inlet tube and an outlet which led first to a dry ice-acetone trap and then to a trap containing a chloroform solution (50-100 ml) of triethylamine (5.5 g, 0.054 mol). Nitrogen was passed through the apparatus for 15 min to purge it of air and the flask contents were then heated in an oil bath at 100-115° in a nitrogen atmosphere until gas evolution ceased (30-75 min). The bath temperature was then raised to 160° to remove volatiles. Nitrogen was passed through the flask as it cooled down, and for an additional hour to aid in the removal of residual volatiles. The triethylamine-chloroform solution, used as a hydrogen chloride trap, was evaporated to dryness and the residue was washed with cold ether. Triethylamine hydrochloride was obtained as an insoluble white solid (20-35% yield, in various runs). The contents of the dry ice trap consisted of two layers, water and a foul smelling oil. Initially the oil was subjected to preparative glc (12% Apiezon L on 60/80 Anakrom ABS, column 5' x 3/8", column temperature 130°); the predominant component consisted of bis-(methylthio)methane (12) (see below for preparation of authentic sample). In subsequent thermolyses, 12 was purified by microdistillation at atmospheric pressure, bp 153°; its yield was about 50%. Nmr ($CDCl_3$) δ 2.17 (s, 6 , $C\underline{H}_3$), 3.67 (s, 2, $C\underline{H}_2$).

Anal. calcd. for $C_3H_8S_2$ (12): C, 33.29; H, 7.45; S, 59.26. Found: C, 33.32; H, 7.45; S, 58.88.

The thermolysis residue, a light brown solid, was dissolved in hot *n*-hexane and the solution was cooled to 0°. The white crystalline precipitate (50% yield), mp 127-127.5°, was recrystallized from *n*-hexane; the solid was identified as bis(N-ethoxycarbonylimino)methane (13), mp 130°, by ir, nmr and mass spectra and mixture melting point with an authentic specimen, mp 131°, prepared from ethyl carbamate and formaldehyde.[17]

Ir (KBr disc) 3360 (s) (N-H stretch), 3000 (w) (C-H stretch), 1690 (s) (C=O) stretch), 1520 (s) (N-H deformation), 1240 (s)(C-O stretch), 1030 (s) (C-N stretch), 1120 (m), 927 (m) and 790 cm^{-1} (w); nmr ($CDCl_3$) δ 5.92 (broad, s, 2, N$\underline{H}$), 4.48 (t, 2, $NC\underline{H}_2N$), 4.10 (q, 4, $C\underline{H}_2CH_3$), 1.20 (t, 6, $CH_2C\underline{H}_3$). The broad singlet at δ 5.92 (position of signal is concentration dependent) disappeared on treatment of the $CDCl_3$ solution of 13 with D_2O containing a trace of CF_3CO_2H.

Anal. calcd. for $C_7H_{14}N_2O_4$ (13): C, 44.20; H, 7.42. Found: C, 44.46; H, 7.43.

The hexane filtrates were evaporated to dryness; the dark residue consisted largely of (13) and ethyl carbamate (7) (glc). Treatment of the residue with chloroform yielded a small quantity of an unidentified insoluble solid, mp ca. 280° dec. It was shown independently that (13) and ethyl carbamate are stable to 160°, the maximum temperature in the thermolysis.

Mass spectrum of (13) (direct insertion at 60°): m/e 190, (0.8), molecular ion $C_7H_{14}N_2O_4$ (15.5 ppm); 161, (34), M-Et, $C_5H_9N_2O_4$ (8.3 ppm); 145, (0.2), M-OEt, $C_5H_9N_2O_3$ (2.7 ppm); 117, (56), m/e 161 - CO_2, $C_4H_9N_2O_2$ (12.4 ppm); 102, (58), m/e 117 - NH, $C_4H_8NO_2$ (10.0 ppm); 90, (4), m/e 117 - HCN, $C_3H_8NO_2$ (0.3 ppm); 89, (11), m/e 117 - C_2H_4, $C_2H_5N_2O_2$ (12.0 ppm); 74, (5), m/e 89 - NH, $C_2H_4NO_2$ (13.8 ppm); 62, (12), m/e 90 - C_2H_4, CH_4NO_2 (15.2 ppm); 58, (7), m/e 120 - CO_2, C_3H_8N (11.7 ppm); 56, (8), m/e 102 - EtOH, C_2H_2NO (12.1 ppm); 45 (14), m/e 89 - CO_2, CH_5N_2 (4.2 ppm); 30, (100), m/e 74 - CO_2, CH_4N (13.9 ppm); 29, (56), C_2H_5 (0.9 ppm); 28, (11), m/e 45 - NH_3, CH_2N (6.0 ppm).

Preparation of Authentic bis(Methylthio)methane (12).[18] Chloromethyl methyl sulfide (9.7 g, 0.10 mol) was added with stirring to water (50 ml) at 4-6° over 35 min. Gas evolution was observed. The reaction mixture was allowed to warm to room temperature and the product was extracted with ether (3 x 50 ml portions). The combined ether extracts were washed sequentially with 10% sodium bicarbonate solution (2 x 50 ml) and water (2 x 50 ml), and dried over anhydrous $MgSO_4$. Filtration and solvent evaporation in a rotary evaporator (water bath 35°) left a clear brown liquid residue (5.3 g, 50%). Distillation through a 7 cm minilab Vigreux column at atmospheric pressure yielded pure 12 (2.9 g, 27%, bp 153°).

Thermolysis of (10). The pure salt (5.76 g, 0.027 mol), mp 98-99° dec, was thermolyzed at 95-100° under nitrogen until gas evolution ceased (ca. 1 hr.), as described above for EMSC (8) except that neat triethylamine was used to trap HCl. Three thermolysis fractions were obtained: (a) cold trap condensate, (b) *precipitate in triethylamine trap, and (c) pot residue.* **Workup of (a):** This was a clear liquid with a strong odor of HCl. It was then allowed to warm slowly to room temperature and the evolved vapors were passed through triethylamine; a white precipitate formed. The residue (1.00 g) was examined by glc (6' x 1/4" Apiezon L on Anakrom ABS column, column temperature 30°). The major component (95%) (retention time 3") was shown by peak enhancement and comparison of its nmr spectrum with that of an authentic sample to be diethyl sulfide (39%). **Workup of (b):** The contents of the triethylamine trap and the triethylamine plus precipitate from the workup of (a) were combined and cold ether (50 ml) was added. The precipitate was filtered, washed with cold ether and dried. It was shown to be triethylamine hydrochloride (1.18 g, mp 253-256°). The yield of HCl was 31%. **Workup of (c):** The pot residue (3.66 g), a black solid, was shaken with chloroform (35 ml) to give a brown solution and an insoluble white solid, mp 270° dec, (0.36 g) (referred to later as d). The solvent was removed from the solution using a rotary evaporator [40° (20 torr)] to give a viscous brown oily residue (2.94 g). Tlc revealed the presence of one major component (R_F 0.65) and four minor components (silica gel 0.25 mm developed with benzene and detected with iodine vapor). The major component was isolated by short path distillation of a portion of the brown oil (1.47 g); it was shown to be ethyl carbamate (52%) by tlc, glc, ir and nmr comparison with an authentic sample. **Workup of (d):** The white solid was insoluble in chloroform, acetone, ethanol, ether, nitromethane, dimethyl sulfoxide and water; it was very slightly soluble in hot nitromethane. A portion of the white solid (0.29 g) was recrystallized from nitromethane to give a white feathery solid, mp 288° dec (0.16 g, 8%). It was identified as 1,1,2,2-tetra(carbethoxyamino)ethane (14) by ir, nmr and chemical ionization mass spectral comparison with an authentic sample[19] and elemental analysis.

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Room Temperature Decomposition of (10) in Chloroform. The salt (2.0 g, 0.0093 mol) was dissolved in chloroform (20 ml) and stirred at 24° for 48 hrs. Evaporation of volatiles [30° (77 torr)] yielded a brown liquid residue. Addition of ether (30 ml) precipitated a small quantity of mauve solid (0.12 g) which was not studied further and a brown solution which yielded a brown residue (1.4 g) on evaporation. Tlc revealed the presence of one major and five minor components (silica gel 0.25 mm, developed with benzene and detected with iodine vapor). Kugelrohr distillation of the brown residue yielded a colorless liquid which solidified. It was identified as ethyl carbamate (75%) by tlc, glc, ir and nmr comparison with an authentic sample.

Thermolysis of 11. A sample of 11 was heated to 150° for 120 min in a slow nitrogen stream; the exit gases were passed through a solution of bromine in carbon tetrachloride (1 g Br_2/25 ml). Gas evolution started almost immediately and was complete in about 90 min; after about 40 min the colorless starting material had turned dark brown. The residue was short-path distilled [bp 73-90° (0.05 torr)] to yield a dark brown residue and a pale yellow odoriferous distillate. Glc analysis (5' x 3/8" 12% Apiezon L on 60/80 Anakrom ABS column, helium flow rate 60 ml/min, column temperature 140°) showed the presence of six components in the distillate of which the two major ones were identified as ethyl carbamate (retention time 1.6", 12.6%) and a previously unreported compound, ethyl N-(ethylthio)carbamate (15) (retention time 8.1", 70%). [Based on 11, the yields (glc) of ethyl carbamate and 15 were 15 and 44%, respectively.] They were separated by preparative glc (conditions as above). Ethyl carbamate was identified by mp and mixture mp, and spectral comparison with an authentic sample. Compound 15 was a colorless liquid with an unpleasant, pungent odor; it was short-path redistilled [bp 90-100° (0.1 torr)] to remove a small quantity of stationary phase with which it was contaminated. Ir (liquid film) 3370 (NH), 1730 (C=O stretch), 1450 (CH_3 and CH_2 deformation), 1220 (C-O stretch), 836

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and 780 cm^{-1}; nmr ($CDCl_3$) δ 5.85 (broad s, 1, N<u>H</u>), 4.17 (q, 2, $CH_3C\underline{H}_2O$, J = 7 cps), 2.74 (q, 2, $CH_3C\underline{H}_2S$, J = 7 cps), 1.81 (t, 3, $C\underline{H}_3CH_2O$, J = 7 cps), 1.67 (t, 3, $C\underline{H}_3CH_2S$, J = 7 cps). The broad singlet at δ 5.85 disappeared on treatment of the nmr solution with D_2O containing a trace of trifluoroacetic acid.

Anal. calcd. for $C_5H_{11}NO_2S$: C, 40.25; H, 7.43; N, 9.39; S, 21.49. Found: C, 40.03; H, 7.28; N, 9.58; S, 21.71.

The bromine-carbon tetrachloride solution was fractionally distilled. After removal of excess bromine and carbon tetrachloride, the residue was subjected to glc analysis (5' x 3/8" 12 % Apiezon L on 60/80 Anakrom ABS column, helium flow rate 60 ml/min, column temperature 110°). The major component (ca. 80%) was identified as 1,2-dibromoethane by comparison of its ir and nmr spectra with those of an authentic sample. Thus the gas evolved in the thermolysis of 11 is ethylene; yields of ethylene trapped ranged from 8-35%.

Attempted Reaction of (11) with Electrophiles. A mixture of EES (3.5 g, 0.02 mol) and acrylonitrile (1.6 g, 0.03 mol) was refluxed under nitrogen for 48 hours; the reaction was monitored by ir. The original carbonyl absorption of EES at 1630 cm^{-1} became less intense with time and virtually disappeared and a new carbonyl band appeared at 1730 cm^{-1}. Micro-distillation of the reaction mixture resulted in almost complete recovery of the acrylonitrile; the product isolated from the residue was ethyl N-(ethylthio)carbamate (15), the thermolysis product of 11 (see above).

Identical results were obtained on refluxing 11 with ethyl acrylate or styrene oxide; 15 was the product isolated and the other components were recovered unchanged.

Attempted Reaction of (9) with Electrophiles. A solution of 9 (1.3 g, 0.009 mol) and p-nitrobenzaldehyde (1.3 g, 0.009 mol) in chloroform (100 ml) was heated under reflux

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for 24 hours. No shift was observed in the carbonyl absorption of 9 at 1620 cm^{-1}; p-nitrobenzaldehyde was recovered unchanged.

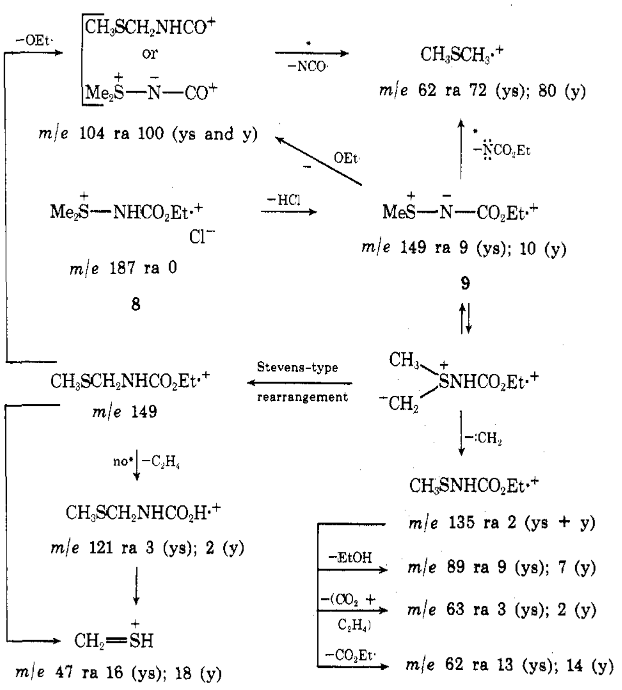
Attempted reaction of 9 with ethyl acrylate and styrene oxide, in the same manner described above for 11, resulted in complete recovery of the electrophiles.

Preparation of N-Ethoxycarbonyliminotriphenylphosphorane (16). A solution of triphenylphosphine (13.1 g, 0.05 mol) in benzene (50 ml) was added dropwise with stirring to a suspension of the sodium salt of ethyl N-chlorocarbamate (6)[14] (7.3 g, 0.05 mol) in benzene (50 ml) at 25-40° over 30 min. The reaction mixture was stirred until a test for positive halogen was negative (total reaction time, about 2 hours). The white insoluble solid was filtered; it was shown to be sodium chloride (2.8 g, 96% yield). The filtrate was evaporated to dryness in a rotary evaporator yielding a white solid residue of crude (16), mp 100-122° (17.1 g). It was purified by recrystallization from ether at -5°; the product had mp 136-7° (overall yield 70%) (lit.[20,21] 135-6°, 136-7°). Ir λ (KBr disc) cm^{-1}; 1640 (C=O stretch), 1600 (C=C), 1445, 1375, 1280, 1120, 1100, 880, 800, 728 and 695 λ nmr ($CDCl_3$) δ 1.23 (t, 3, $C\underline{H}_3CH_2O$), 4.12 (q, 2, $CH_3C\underline{H}_2O$), 7.65 (m, 15, aromatic).

Attempted Reaction of (16) with Electrophiles. A solution of 16 (3.5 g, 0.01 mol) and benzaldehyde (1.5 g, 0.015 mol)) in THF (50 ml) was refluxed for 24 hours. The solvent was removed by vacuum evaporation and the residue was filtered. The white solid was washed with a small quantity of cold ether; it was identified as unreacted EPP (3.4 g, 97% recovery) by mixture melting point and ir.

A solution of 16 (3.5 g, 0.01 mol) and styrene oxide (2.4 g, 0.02 mol) in DMF (50 ml) was refluxed for 24 hours. The solution was concentrated under vacuum to about 1/4 its volume and then cooled to 0°. The white precipitate was filtered off and washed with a small quantity of cold ether; it was identified as unreacted 16 (3.1 g, 91% recovery)

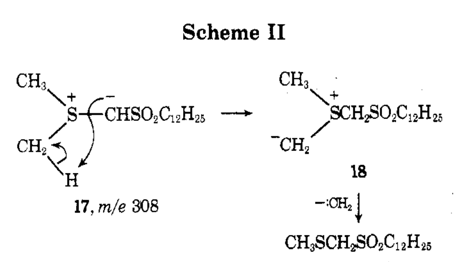
Scheme I[a]



[a] ys = ylide salt 8; y = ylide 9; ra = relative abundance.

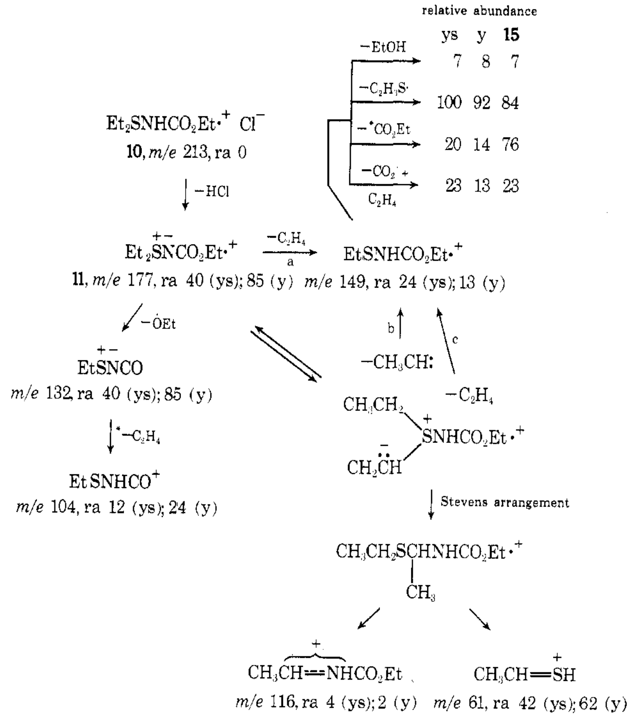
lecular ion at *m/e* 308 and the primary fragmentation process is initial loss of methylene to give an ion (19) with *m/e* 294. The intermediacy of the sulfurane 18 was involved to rationalize the results (Scheme II).

Scheme II



Mass Spectral Fragmentation of 10 and 11. The mass spectral fragmentation patterns of ylide salt 10 and ylide 11 are also very similar; they are summarized in a superimposed, condensed version in Scheme III. As with 8 (Scheme I), primary fragmentation of 10 is loss of HCl to give the iminosulfurane 11. The formation of the ion with *m/e* 149 can then occur in three ways: (a) direct loss of ethylene from 11, (b) loss of CH_3CH: from the sulfurane, and (c) loss of ethylene from the sulfurane. It is not possible to deduce from the mass spectrum which pathway (or pathways) leads to the fragment with *m/e* 149. The subsequent fragmentation of the ion with *m/e* 149 is in excellent qualitative agreement with that observed for the pure compound, 15, thus adding credibility to its postulated intermediacy in the fragmentation of 11. It is also likely that the intermediate sulfurane undergoes a Stevens-type rearrangement to ethyl *N*-(1-ethylthioethyl)carbamate, fragmentation of which accounts for fragments with *m/e* 116 and 61.

Scheme III[a]



[a] ys = ylide salt 10; y = ylide 11; ra = relative abundance; * = metastable ion.

Although the mass spectra of 10 and 11 are very similar, their thermolysis products are quite different.

Attempted Reaction of Iminosulfuranes with Electrophiles. Iminosulfuranes **8** and **11** are isoelectronic with sulfur–carbon ylides (sulfuranes). We therefore examined the reactions of **8** and **11** with selected electrophiles with the object of developing new, mild synthetic pathways in neutral media for the formation of heterocyclic ring systems (oxaziranes and aziridines), analogous to the syntheses of epoxides and cyclopropanes from sulfur ylides and carbonyls[26-29] and activated α,β-unsaturated compounds,[30] respectively.

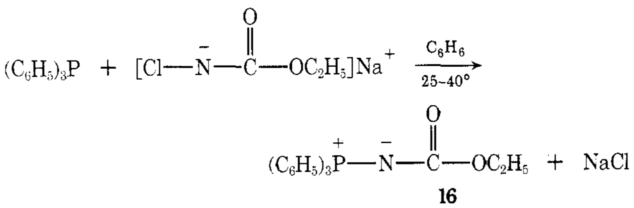
Neither **8** nor **11** reacted with excess neat acrylonitrile, ethyl acrylate, or styrene oxide up to the reflux temperatures of the system. Furthermore, when equimolar proportions of *p*-nitrobenzaldehyde and ylide were dissolved in chloroform and heated under reflux, there was also no reaction. The electrophiles were recovered and, in reactions of **11** at elevated temperatures, ethyl *N*-(ethylthio)carbamate (**15**), the anticipated thermolysis product, was also isolated in good yield. Failure of **8** and **11** to react is interpreted to mean that the nucleophilicity of nitrogen is extensively reduced owing to delocalization of the negative charge into the ester moiety.

The striking difference in reactivity between iminosulfuranes and sulfuranes prompted us to examine the reactivity of an iminophosphorane, structurally similar to the iminosulfuranes, with electrophiles. Chemical properties of iminophosphoranes are reported to be similar to those of the isoelectronic phosphorus ylides, although literature information on the former is considerably sparser.[4] The outstanding property of phosphorus ylides is their nucleophilicity, which permits a wide range of useful synthetic reactions to be carried out, of which the Wittig reaction is perhaps the most important.

Iminophosphoranes have been shown to react with carbonyl compounds to form Schiff bases and phosphine oxide, analogous to the Wittig olefin-synthesis reaction, as illustrated by the reaction of *N*-phenyliminotriphenylphosphorane with diphenylketene to yield triphenylketenimine.[31] Benzaldehyde, benzophenone, and phenyl isocyanate behave similarly and, in essence, involve the replacement of a carbonyl oxygen by the *N*-phenylimino group.

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{N}-C_6H_5 + (C_6H_5)_2C{=}C{=}O \longrightarrow (C_6H_5)_2C{=}C{=}NC_6H_5 + (C_6H_5)_3PO$$

Accordingly, we prepared the known *N*-ethoxycarbonyliminotriphenylphosphorane[20,21] (**16**), mp 136°, from the sodium salt of ethyl *N*-chlorocarbamate (**6**) and triphenyl phosphine in benzene. The ir of **16** (KBr disk) shows strong carbonyl absorption at a low frequency of 1640 cm^{-1}, as is also observed with the iminosulfuranes, suggesting the same type of charge delocalization. Reaction of **16** with benzaldehyde in refluxing tetrahydrofuran or with styrene oxide in refluxing dimethylformamide, both for 24 hr, yielded unreacted **16** (91–97%). Similar results were obtained without solvent. Thus **16** is also unreactive and, we conclude, for the same reason, that **8** and **11** are unreactive to electrophiles.



$$(C_6H_5)_3P + [Cl-\overset{-}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5]Na^+ \xrightarrow[25-40^\circ]{C_6H_6} (C_6H_5)_3\overset{+}{P}-\overset{-}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + NaCl$$

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Registry No.—**6**, 16844-21-6; **7**, 51-79-6; **8**, 29548-68-3; **9**, 29548-70-7; **10**, 29548-69-4; **11**, 29548-71-8; **12**, 1618-26-4; **13**, 3693-53-6; **14**, 17350-57-1; **15**, 51552-67-1; **16**, 17437-51-3.

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(2) Participant in the Chemistry Honors Undergraduate Research Program, Temple University.

(3) We prefer the name "iminosulfuranes" following the usage in a recent book.[4] Such nomenclature is not only convenient and focuses attention on the tetracovalent nature of sulfur but is also consistent with that of the corresponding P–N ylides called "iminophosphoranes" and conforms to the designation of Wittig reagents as "phosphoranes." The term "sulfilimines" is used by *Chemical Abstracts* but other names appear in the recent literature, for example, "sulfinimines" and "sulfimides."

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