ppm); 132 (15), M − [HBr + CH_3·], $C_5H_{10}NOS$ (1.4 ppm); 119 (8), *m/e* 147 − C_2H_4 and M − C_2H_5Br, C_4H_9NOS (4.8 ppm); 110 (42), $C_2H_5{}^{81}Br$ (62.8 ppm); 108 (38), $C_2H_5{}^{79}Br$ (3.4 ppm); 104 (10), *m/e* 119 − CH_3·, C_3H_6NOS (67.3 ppm); 90 (15), *m/e* 132 − NCO·, $C_4H_{10}S$ (32.2 ppm); 89 (18), *m/e* 147 − NHCO-CH_3· and *m/e* 132 − HNCO, C_4H_9S (32.6 ppm); 86 (10), *m/e* 147 − EtS·, C_4H_8NO (40.7 ppm); 82 (28), $H^{81}Br$ (0 ppm); 81 (11), ^{81}Br (11.1 ppm); 80 (32), $H^{79}Br$ (76.4 ppm); 79 (11), ^{79}Br (57.0 ppm); 77 (67), *m/e* 119 − ketene, C_2H_7NS (24.2 ppm); 76 (13), *m/e* 104 − CO, C_2H_6NS (3.1 ppm); 62 (14), *m/e* 104 − NCO· and *m/e* 90 − C_2H_4, C_2H_6S (9.4 ppm); 62 (17), *m/e* 104 − ketene, CH_4NS (13.3 ppm); 61 (44), *m/e* 104 − HNCO and *m/e* 89 − C_2H_4, C_2H_5S (59.0 ppm); 60 (14), *m/e* 77 − NH_3, C_2H_4S (41.6 ppm); 60 (64), *m/e* 86 − C_2H_2, C_2H_6NO (41.6 ppm); 59 (26), *m/e* 119 − C_2H_4S, C_2H_5NO (32.8 ppm); 49 (52), *m/e* 77 − C_2H_4, H_3NS (47.7 ppm); 48 (11), *m/e* 76 − C_2H_4, H_2NS (32.2 ppm); 44 (2), *m/e* 86 − ketene, C_2H_6N (21.3 ppm); 43 (89), CH_3CO (35.5 ppm); 41 (17), C_2H_3N (73.2 ppm); 29 (100), C_2H_5 (65.2 ppm); 28 (53) (doubly ionized), C_4H_8 (22.2 ppm).

Results with **4c**: *m/e* 147 (10), M − HCl, $C_6H_{13}NOS$ (7.4 ppm); 132 (43), *m/e* 147 − CH_3, $C_5H_{10}NOS$ (2.9 ppm); 119 (14), *m/e* 147 − C_2H_4, C_4H_9NOS (5.6 ppm); 104 (23), *m/e* 119 − CH_3, C_3H_6NOS (0.5 ppm); 90 (11), *m/e* 132 − NCO, $C_4H_{10}S$ (10.4 ppm); 89 (34), *m/e* 147 − $NHCOCH_3$ and *m/e* 132 − HNCO, C_4H_9S (9.6 ppm); 86 (17), *m/e* 147 − EtS, C_4H_8NO (0.8 ppm); 77 (81), *m/e* 119 − ketene, C_2H_7NS (5.6 ppm); 76 (31), *m/e* 104 − CO, C_2H_6NS (6.4 ppm); 76 (12), *m/e* 104 − C_2H_4, CH_2NOS (2.4 ppm); 75 (14), *m/e* 90 − CH_3, C_3H_7S (3.6 ppm); 62 (12), *m/e* 104 − NCO and *m/e* 90 − C_2H_4, C_2H_6S (46.8 ppm); 62 (18), *m/e* 104 − ketene, CH_4NS (36.3 ppm); 61 (69), *m/e* 104 − HNCO and *m/e* 89 − C_2H_4, C_2H_5S (27.3 ppm); 60 (11), *m/e* 77 − NH_3, C_2H_4S (28.3 ppm); 60 (57), *m/e* 86 − C_2H_2, C_2H_6NO (28.0 ppm); 59 (3), *m/e* 119 − C_2H_4S and *m/e* 147 − C_4H_8S, C_2H_5NO (28.5 ppm); 49 (51), *m/e* 77 − C_2H_4, H_3NS (13.5 ppm); 48 (20), *m/e* 76 − CO and *m/e* 76 − C_2H_4, H_2SN (8.5 ppm); 47 (12), *m/e* 62 − CH_3, CH_3S (5.1 ppm); 45 (9), *m/e* 62 − NH_3 and *m/e* 60 − CH_3, CHS (16.1 ppm); 44 (2), *m/e* 86 − ketene, C_2H_6N (21.1 ppm); 43 (90), *m/e* 119 − EtSNH, CH_3CO (25.3 ppm); 41 (23), C_2H_3N (49.0 ppm); 38 (24), $H^{37}Cl$ (52.7 ppm); 36 (73), $H^{35}Cl$ (62.3 ppm); 29 (48), C_2H_5 (32.9 ppm); 28 (54), C_2H_4 (39.7 ppm).

Registry No.—**2a**, 32805-43-9; **2b**, 33707-44-7; **2c**, 32805-46-2; **2d**, 33707-46-9; **2e**, 33707-47-0; **2f**, 33707-48-1; **3a**, 32805-42-8; **3b**, 33707-49-2; **3c**, 32805-45-1; **3d**, 33707-50-5; **3e**, 33707-51-6; **3f**, 33707-52-7; **4a**, 32805-44-0; **4c**, 32805-47-3.

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Iminosulfuranes (Sulfilimines). V.[1a] Thermolysis of *N*-Acetyliminodialkylsulfuranes[1b]

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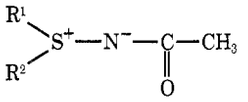
The thermolysis of *N*-acetyliminodialkylsulfuranes, $R^1R^2S^+N^-COCH_3$ ($R^1 = CH_3$, $R^2 = C_2H_5$; $R^1 = R^2 = C_2H_5$; $R^1 = R^2 = n\text{-}C_3H_7$; $R^1 = R^2 = i\text{-}C_3H_7$), in xylene affords olefin (ethylene or propylene) and *N*-(alkylthio)acetamides, $RSNHCOCH_3$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$), a series of new compounds. When thermolysis is carried out without solvent, intermolecular reactions also occur. In the case of the dimethyl ylide, thermolysis products include dimethyl sulfide, bis(methylthio)methane, *N*,*N*′-methylenebisacetamide, and *N*,*N*′,*N*″-methylidenetrisacetamide. A mechanism involving a Pummerer type rearrangement is proposed to account for those reaction products.

The thermolysis of *N*-ethoxycarbonyliminodialkylsulfuranes (**1**)[2] and *N*-tosyliminosulfuranes (**2**)[3] with β-hydrogen atoms has been reported. The primary reaction is the elimination of olefin (Scheme I) and it has been rationalized by a mechanism involving a five-center transition state (Scheme I; per cent yields in parentheses).

In this paper, we describe the results of the thermolysis in xylene of *N*-acetyliminodialkylsulfuranes (**3b–e**) containing hydrogen atoms β to the sulfur atom. For purposes of comparison, the thermolysis of the dimethyl ylide, **3a**, which does not have β hydrogens, was also examined both with and without solvents. Possible reaction pathways are also discussed.

Results and Discussion

The iminosulfuranes **3b–e**, prepared as described in the previous paper,[1a] were heated in refluxing xylene for 2.5 hr. The olefin evolved (ethylene or propylene) was trapped in Br_2–CCl_4 solution, and the *N*-(alkylthio)acetamides (**4**) ($R^1SNHCOCH_3$, R^1 = CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$) were isolated by distillation of the reaction mixture. The *N*-(alkylthio)acetamides **4** have not been reported previously; their structures were established by ir, nmr, and microanalysis. The results of the thermolysis are summarized in Table I; a typical reaction pathway for thermolysis in refluxing xylene is shown in Scheme II, path a.



3a, $R^1 = R^2 = CH_3$
b, $R^1 = CH_3$; $R^2 = C_2H_5$
c, $R^1 = R^2 = C_2H_5$
d, $R^1 = R^2 = n\text{-}C_3H_7$
e, $R^1 = R^2 = i\text{-}C_3H_7$

In the case of iminosulfurane **3b**, the lower yield of **4** (R^1 = CH_3) may be explained by the presence of fewer β hydrogens. In this case a small amount of *N*,*N*′-methylenebisacetamide, $CH_2(NHCOCH_3)_2$ (yield 3%), is also obtained. This is assumed to be formed by

(1) (a) For the previous paper, see *J. Org. Chem.*, **37**, 1121 (1972). (b) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Apr 1971. Preliminary publication: *Tetrahedron Lett.*, 1761 (1971). (c) Postdoctoral Fellow from the University of Tokyo. (d) Postdoctoral Fellow from the University of London.

(2) G. F. Whitfield, H. S. Beilan, D. Saika, and D. Swern, *Tetrahedron Lett.*, 3543 (1970).

(3) S. Oae, K. Tsujihara, and N. Furukawa, *ibid.*, 2663 (1970).

SCHEME I

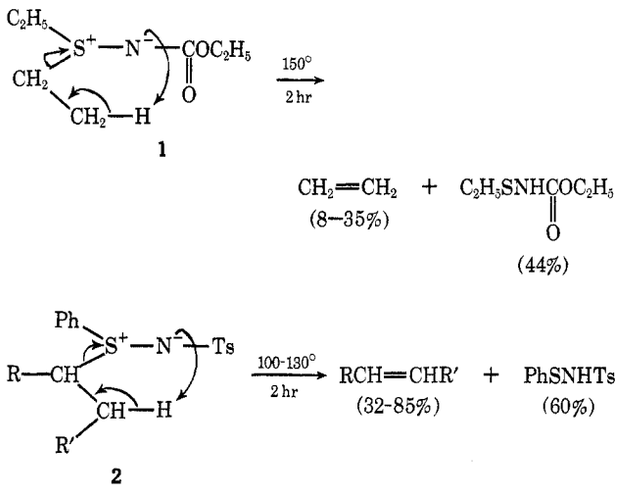


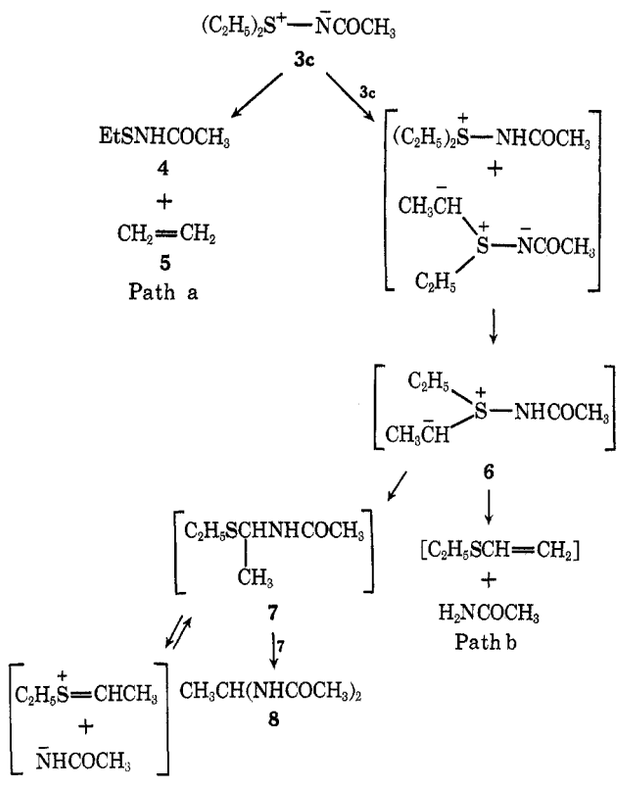
TABLE I

THERMOLYSIS OF *N*-ACETYLIMINODIALKYLSULFURANES, $R^1R^2S^+—N^-COCH_3$, IN REFLUXING XYLENE

	Iminosulfurane[a] R¹	R²	Olefin (yield, %)	R¹SNHCOCH₃ (4) Yield, % Crude	Pure	Bp,[b] °C, at 0.03mm
3b	CH_3	C_2H_5	$CH_2=CH_2$ (44)	50	30	64–65
3c	C_2H_5	C_2H_5	$CH_2=CH_2$ (51)	95	75	72–74
3d	*n*-C_3H_7	*n*-C_3H_7	$CH_3CH=CH_2$ (25)	85	55	77–78
3e	*i*-C_3H_7	*i*-C_3H_7	$CH_3CH=CH_2$ (58)	95	70	83–85

[a] Satisfactory analyses (±0.3%) for C, H, N, and S were obtained for all new compounds listed: Ed. [b] Measured in a capillary.

SCHEME II



a mechanism similar to that proposed for the thermolysis of **3a**, as discussed later.

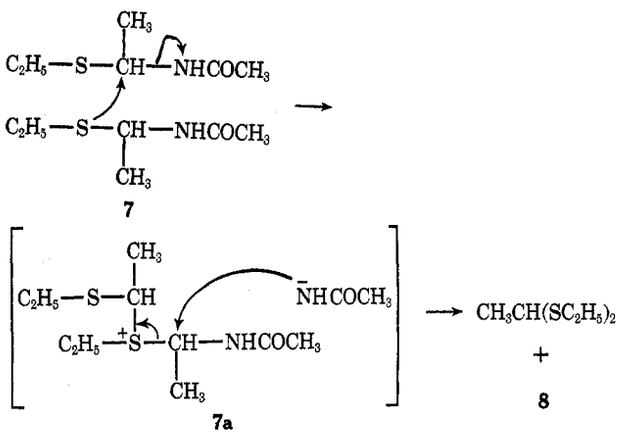
Thermolysis of iminosulfurane **3c** without solvent at 140–145° gives **5** (30%) and **4** ($R^1 = C_2H_5$) (46%) (Scheme II, path a); in addition, acetamide (29%), *N,N'*-ethylidenebisacetamide (**8**) (2%), and an unsaturated sulfide suspected to be ethyl vinyl sulfide are also formed (path b). Since pure **4** ($R^1 = C_2H_5$) is stable at the thermolysis temperature [only about 10% of **4** ($R^1 = C_2H_5$) decomposes at 140–145° in 2.5 hr], it is apparent that **4** ($R^1 = C_2H_5$) is not the intermediate for acetamide and unsaturated sulfide.

A possible mechanism for pyrolysis in the absence of solvent is shown in Scheme II, path b; the formation of the ylide **6**, and the subsequent cleavage of the S–N bond by a five-center transition state, is similar to that proposed for the formation of **4** and **5**.

Since acetamide and unsaturated sulfide are not obtained by thermolysis in xylene, it seems likely that path b is an intermolecular process. We assume that the primary step is protonation of the nitrogen atom of the iminosulfurane **3c** by another molecule of **3c**, followed by a second transfer of a proton from a methylene group to give **6**.

The formation of *N,N'*-ethylidenebisacetamide (**8**) is especially interesting since in the thermolysis of the analogous dimethyliminosulfurane (**3a**) (Scheme IV), *N,N'*-methylenebisacetamide (**10**) is a major product. The formation of **8** may be rationalized by the rearrangement of the ylide **6** to the sulfide **7**, followed by nucleophilic attack of acetamide anion at the methine carbon of **7**. An alternative pathway (Scheme III)

SCHEME III



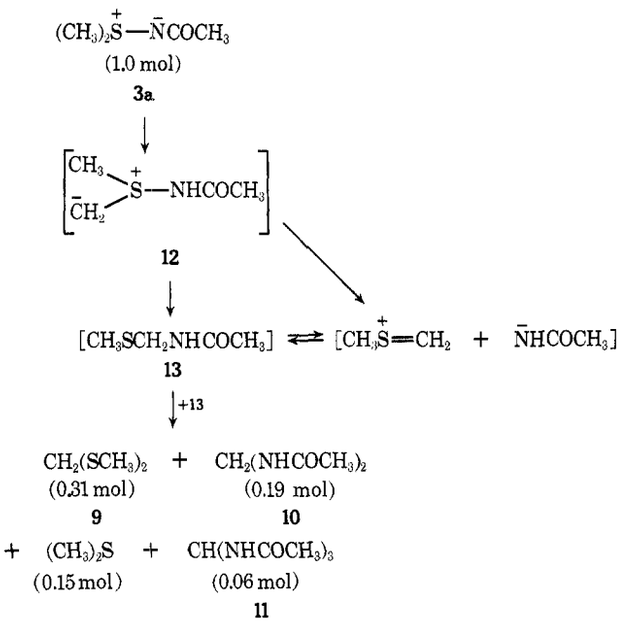
for formation of **8** may involve nucleophilic attack of the sulfur atom of **7** on the methine carbon of another molecule of **7** giving the sulfonium salt **7a**. Subsequent decomposition of **7a** would cause bond cleavage between sulfur and carbon to give **8**. 1,1-Bis(ethylthio)ethane was not isolated; we invoke this compound as the other product on the basis of the isolation of bis(methylthio)methane in the thermolysis of the dimethyl ylide **3a** (Scheme IV).

As shown in our previous paper,[1a] the mass spectrum of the iminosulfurane **3c** shows that the primary fragmentations involve elimination of ethylene to give the radical ion of **4** ($R^1 = C_2H_5$) and rearrangement of **3c** possibly to the sulfide **7**. These processes are very similar to the thermolysis of **3c**, shown in Scheme II.

Similarities between mass spectral fragmentation and thermolysis are also observed with the dimethylsulfurane **3a**.

Thermolysis of the iminosulfurane **3a** without solvent at 120–125° for 24 hr gives bis(methylthio)-methane (**9**), *N*,*N'*-methylenebisacetamide (**10**), dimethyl sulfide, and *N*,*N'*,*N''*-methylidenetrisacetamide (**11**) (Scheme IV, molar yields in parentheses). The material balance was 66%. All the products have been isolated and identified by ir, nmr, and microanalysis and by comparison with authentic samples.

SCHEME IV



A pathway is proposed which involves the rearrangement of **3a** to *N*-(methylthiomethyl)acetamide (**13**) *via* the ylide **12**. The formation of sulfurane **12** may be facilitated by resonance stabilization involving $d\pi$ bonding between sulfur and carbon atoms. Subsequent rearrangement of **12** would give **13**. This process is very similar to the reaction of dimethyl sulfoxide with acetic anhydride (Pummerer rearrangement) to give α-acetoxymethylthiomethane.[4,5]

The subsequent partial dissociation of **13** and nucleophilic attack of the acetamide ion on the methylene group of **13** would give **9** and **10**. The pathways for formation of dimethyl sulfide and the minor product (**11**) are not evident; **11** probably comes from **10**.

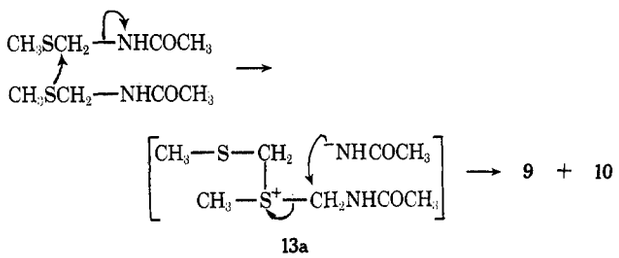
An alternative pathway for the formation of **9** and **10** would involve nucleophilic attack of the sulfur atom in **13** on the methylene carbon of another molecule of **13**, giving the sulfonium salt **13a** (Scheme V). Subsequent decompsosition of **13a** would cause bond cleavage between sulfur and carbon to give **9** and **10**.

Another pathway (Scheme VI) leading to **9** and **10** from **13** involves a four-center transition state and does not require the discrete existence of the acetamide anion.

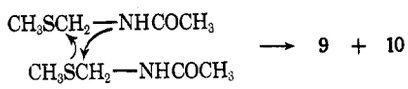
As mentioned in our previous paper,[1a] the mass spectral fragmentation of the iminosulfurane **3a** affords the ions at *m/e* 61 (C_2H_5S) and 72 (C_3H_6NO), which

(4) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **626**, 19 (1959).
(5) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).

SCHEME V



SCHEME VI

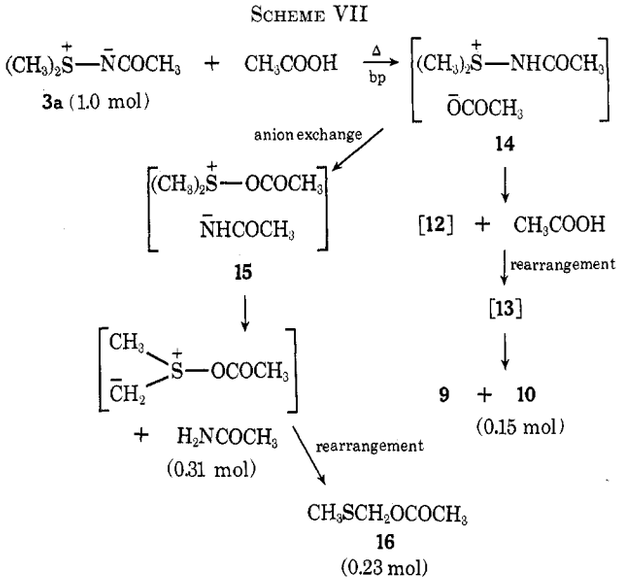


may arise by fragmentation of **13** (formed by rearrangement of **3a**). Thus, there appear to be certain similarities between the thermolysis of **3a** and its behavior on electron impact.

In contrast, when **3a** is heated in refluxing toluene for 24 hr, more than 90% of **3a** is recovered. This suggests that the rearrangement of **3a** to **13** (Scheme IV) is an intermolecular process. The situation is quite similar to the thermolysis of diethylsulfurane **3c** without solvent, as already mentioned (Scheme II, path b). Again, the first step may be a proton transfer from one molecule of **3a** to another molecule of **3a**, followed by a second proton transfer to yield **12**. If this process is correct, it would be expected that a protic acid would catalyze the reaction, thus accelerating rearrangement of **3a** to **13**.

When thermolysis of **3a** is conducted in refluxing acetic acid, the reaction rapidly affords **9** and **10**, along with **16** and acetamide. The reactions have been rationalized in Scheme VII (molar yields in parentheses).

SCHEME VII



In this case, the first step may be the formation of sulfonium salt **14**, which is followed by either proton abstraction by the anion to give the ylide **12** or the exchange of the anion to give another sulfonium salt **15**. Rearrangement of **12** to **13** and the subsequent intermolecular reaction would give the final products

TABLE II
IR AND NMR OF N-(ALKYLTHIO)ACETAMIDES (4), $R^1SNHCOCH_3$

	Ir, cm^{-1}[a]			Nmr[b]				
R^1	ν_{NH}	ν_{CO}	ν_{CN}	NH	CH_3CO	α-CH	β-CH	γ-CH
CH_3	3250	1660	1240	6.50 (bs)	2.10 (s)	2.38 (s)		
C_2H_5	3240	1660	1240	7.59 (bs)	2.16 (s)	2.77 (q) (J = 8 Hz)	1.26 (t) (J = 7 Hz)	
n-C_3H_7	3250	1670	1245	7.16 (bs)	2.09 (s)	2.67 (t) (J = 7 Hz)	1.61 (se) (J = 8 Hz)	0.97 (t) (J = 7 Hz)
i-C_3H_7	3250	1675	1240	7.43 (bs)	2.10 (s)	3.17 (m)	1.18 (d) (J = 6 Hz)	

[a] Liquid film. [b] Parts per million from TMS in $CDCl_3$ at 37°. Integrations were in accord with the proposed structures; s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, se = sextet, and m = multiplet.

9 and **10**. The sulfonium salt **15** could follow a similar process to yield acetamide and **16**.

Experimental Section

Ir, Nmr, and Glc.—Ir spectra were obtained as KBr discs or liquid films using a Perkin-Elmer infrared spectrophotometer, Model 137B. Nmr spectra were obtained with a Varian A-60A spectrometer. Gas chromatographic analyses were performed on a Wilkens Aerograph A 90-P3 using a 5 ft × 1/4 in. column packed with 15% Carbowax on Chromosorb W, carrier gas He, column temperature 110°.

Thermolysis of 3c.—Pure **3c** (2.16 g, 0.0147 mol) was dissolved in xylene (40 ml) and the mixture was refluxed for 2.5 hr. Ethylene was trapped in Br_2 (1.5 ml, 0.029 mol/25 ml of CCl_4) solution. The amount of 1,2-dibromoethane was determined by nmr using benzene as an internal standard. Xylene was distilled off under vacuum at room temperature, and a pale yellow oil was obtained as a residue. It was found to be almost pure *N*-(ethylthio)-acetamide, **4** (R^1 = C_2H_5), by nmr and tlc. Analytically pure **4** (R^1 = C_2H_5) was obtained by fractional distillation under vacuum.

Thermolysis of the other iminosulfuranes (**3b**, **3d**, and **3e**) was carried out in a similar manner. Ir and nmr of **4** are summarized in Table II.

The thermolysis of **3c** without solvent was carried out as follows: **3c** (6.37 g, 0.0432 mol) was placed in a flask equipped with a gas inlet and a condenser which was connected to a cold trap (−78°) and then to a trap containing Br_2 (3.0 ml, 0.058 mol/25 ml of CCl_4). The iminosulfurane **3c** was heated under a dry nitrogen stream at 140–145° for 2.5 hr. After the reaction, the Br_2/CCl_4 trap was removed and the reaction system was evacuated to 0.2–0.3 mm at room temperature for 2 hr. A clear liquid (0.60 g) condensed in the cold trap and a dark-colored pot residue (3.74 g) was obtained. The yield of 1,2-dibromoethane in the Br_2/CCl_4 trap was determined by the method described above.

Examination by glc showed that the cold trap condensate had two major components, one of which had almost the same retention time as did diethyl sulfide, but its nmr indicated that it contained a vinyl group; it was assumed to be ethyl vinyl sulfide. An attempt to separate this component by preparative glc was unsuccessful, probably because of polymerization on the column. Another fraction in the cold trap condensate was separated by preparative glc. It gave an ir spectrum very similar to that of diethyl disulfide, but it was also found by nmr to have a vinyl group. The fraction appears to consist of more than two components, but they could not be separated and identified. The nmr spectrum of the pot residue showed that it consisted mainly of the acetamide **4** (R^1 = C_2H_5) and unreacted **3c**, and their amounts could be estimated by nmr band intensities. Pure acetamide and **4** (R^1 = C_2H_5) were obtained by vacuum distillation. *N*,*N*′-Ethylidenebisacetamide (**8**) [0.0678 g, mp 169–170° (lit.[6] 180°)] was obtained by crystallization of the pot residue from $CHCl_3$–Et_2O: ir (KBr disc) 3240 (NH stretch), 1630 (CO stretch), 1560, and 1520 cm^{-1} (NH deformation and CN stretch); nmr (from TMS in DMSO-d_6) 1.23 (d, J = 7 Hz, CH_3CH–), 1.78 (s, CH_3CO–), 5.44 (m, CH_3CH–), 8.09 ppm (d, J = 7 Hz, –NH–).

Thermolysis of 3a.—The iminosulfurane **3a** (2.60 g, 0.0218 mol) was placed in a flask equipped with a gas inlet and a reflux condenser which was connected to a cold trap (−78°). The flask was heated at 120–125° for 24 hr under a dry N_2 stream. Dimethyl sulfide (0.20 g, 0.0032 mol) was obtained in the cold trap. The cold trap was replaced by another one, and the reaction system was evacuated to about 1 mm at room temperature. A clear liquid was then obtained. It was identified as bis(methylthio)methane (**9**) (0.74 g, 0.0068 mol) by comparison with an authentic sample:[7] nmr (from TMS in DMSO-d_6) 2.08 (s, CH_3S–), 3.71 (s, $-CH_2-$). The pot residue was washed with hot acetone; the acetone-insoluble compound was found to be *N*,*N*′,*N*″-methylidenetrisacetamide (**11**) (0.26 g, 0.0014 mol): mp 262–264° (lit.[8] 261°); ir (KBr disc) 3250 (NH stretch), 1650 (CO stretch), 1520 (NH deformation and CN stretch).

Anal. Calcd for $C_7H_{13}N_3O_3$: C, 44.90; H, 7.01; N, 22.45. Found: 44.68; H, 7.27; N, 22.50.

An authentic sample of **11** was prepared from acetamide and acetic anhydride.[8] *N*,*N*′-Methylenebisacetamide (**10**) was obtained from the acetone-soluble portion of the pot residue by crystallization (0.52 g, 0.0040 mol): mp 200° (lit.[9] 200°); ir (KBr disc) 3200 (NH stretch), 1640 (CO stretch), 1540 cm^{-1} (NH deformation and CN stretch); nmr (from TMS in DMSO-d_6) 1.86 (s, CH_3CO–), 4.46 (t, J = 6 Hz, $-CH_2-$), 8.54 ppm (broad s, –NH–).

Anal. Calcd for $C_5H_{10}N_2O_2$: C, 46.13; H, 7.76; N, 21.53. Found: C, 46.37; H, 7.88; N, 21.49.

A solution of **3a** (3.10 g, 0.0260 mol) in toluene (80 ml) was refluxed for 24 hr. Most of the solvent was distilled off and the residual solution was then cooled to −15°. Unreacted **3a** was recovered as a precipitate (2.85 g, 92% of starting amount).

Reaction of 3a with Acetic Acid.—A preliminary test by nmr showed that when **3a** was heated in acetic acid, almost all of it had reacted within 3.5 hr, giving **9**, **10**, **16**, and presumably acetamide also. The relative amounts of **16**:**9** or **10** was about 3.5. Products were identified by comparison of their spectral properties with those of authentic samples. Preparatively, a solution of **3a** (3.40 g, 0.0285 mol) in acetic acid (80 ml) was refluxed for 3 hr. Most of the acetic acid was then distilled off, and the residue was distilled under vacuum. A mixture of acetic acid and **16** was obtained as a distillate; the amount of **16** was estimated by nmr (0.00664 mol). The pot residue was washed with warm ether and **10** was isolated as a precipitate (0.533 g, 0.00425 mol). The ether was distilled from the filtrate and the residue was recrystallized from $CHCl_3/CCl_4$ to give acetamide (0.54 g, 0.00915 mol). An authentic sample of **16** was prepared by reaction of dimethyl sulfoxide with acetic anhydride.[4]

Registry No.—**4** (R^1 = CH_3), 33707-40-3; **4** (R^1 = C_2H_5), 33815-39-3; **4** (R^1 = n-C_3H_7), 33707-41-4; **4** (R^1 = i-C_3H_7), 33707-42-5; **8**, 5335-91-1; **9**, 1618-26-4; **10**, 2852-14-0; **11**, 29284-49-9.

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(6) H. Böhme and G. Berg, *Chem. Ber.*, **99**, 2127 (1966).

(7) H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949).

(8) H. Bredereck, R. Gompper, F. Effenberger, H. Keck, and H. Heise, *Chem. Ber.*, **93**, 1398 (1960).

(9) H. Reimlinger, *ibid.*, **92**, 970 (1959).