n-propylthioallyllithium, 33527-76-3; trityllithium, 733-90-4; cis-4,4,4-triphenyl-1-mercapto-2-butene, 33608-39-8; trans-4,4,4-triphenyl-1-mercapto-2-butene, 33531-84-9; tritylpotassium, 1528-27-4; 4,4,4-triphenylbutanal (2,4-DNPH derivative), 33527-79-6; potassium dimsylate, 17609-15-3.

Iminosulfuranes (Sulfilimines). IV.[1a] The Preparation and Properties of N-Acetyliminodialkylsulfuranes[1b]

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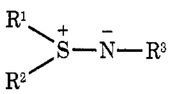
N-Acetyliminodialkylsulfonium bromides, $(R^1R^2S^+NHCOCH_3)Br^-$ [$R^1 = R^2 = CH_3$; $R^1 = CH_3$, $R^2 = C_2H_5$; $R^1 = R^2 = C_2H_5$; $R^1 = R^2 = n\text{-}C_3H_7$; $R^1 = R^2 = i\text{-}C_3H_7$; $R^1, R^2 = -(CH_2)_4-$], were prepared in 38–81% yields by the reaction of N-bromoacetamide with alkyl sulfides in a mixture of CCl_4 and acetone. The sulfonium bromides were converted in excellent yields (88–98%) to the N-acetyliminodialkylsulfuranes, $R^1R^2S^+N^-COCH_3$, by treatment with triethylamine in methylene chloride. Some N-acetyliminodialkylsulfonium chlorides were also prepared. Spectroscopic data show that the iminosulfuranes have extensive charge delocalization over the SNCO system, and the S–N bond is considered to be semipolar. The first detailed mass spectral fragmentation of iminosulfuranes and their salts is reported.

The nature of the N substituent in iminosulfuranes (**1**) has a significant effect on the polarity of the sulfur-



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nitrogen bond and hence on their reactivity. Iminosulfuranes with alkyl,[2] aryl,[3] halogen,[4] nitrile,[5] carboethoxy,[6] sulfonyl,[7] benzoyl,[8] and halogenated acetyl[9] groups on the nitrogen atom are known.

N-(Haloacetyl)iminosulfuranes have also been prepared by the condensation of di- and trichloroacetylisocyanates with dimethyl sulfoxide,[10] and by the reaction of α-dichloro- and α-dibromoacetamide with sulfides in the presence of sodium hypochlorite.[11]

In 1947, Likhosherstov[12] reported that N-chloroacetamide reacts with dimethyl sulfide in CCl_4–acetone solution to give N-acetyliminodimethylsulfonium chloride, a compound which could not be obtained pure and was highly sensitive to moisture. Treatment of the sulfonium chloride with ammonia was reported to give an oil, suspected to be N-acetyliminodimethylsulfurane. The iminosulfurane was not purified nor was its structure established.

We report here (a) the first preparations of pure N-acetyliminodialkylsulfuranes by a modification and improvement of Likhosherstov's method and (b) establishment of their structure by ir, nmr, uv, and mass spectrometry. This is the first in a series of papers in which the effects of the substituent on nitrogen on reactivity, nucleophilicity, basicity, and spectral properties of iminosulfuranes are being systematically explored.

Results and Discussion

Preparation of N-Acetyliminodialkylsulfuranes and Their Salts.—The synthetic route used is shown in Scheme I (yields in parentheses).

SCHEME I

$$R^1R^2S + \underset{(NBA)}{BrNHCOCH_3} \xrightarrow{0°} \underset{\mathbf{3}\ (38\text{–}81\%)}{R^1R^2\overset{+}{S}NHCOCH_3\ Br^-} \underset{HBr,\ 0°}{\overset{(C_2H_5)_3N,\ 0°}{\rightleftarrows}}$$

$$\underset{\mathbf{2}\ (88\text{–}98\%)}{R^1R^2\overset{+}{S}\overset{-}{N}COCH_3} \xrightarrow{HCl,\ 0°} \underset{\mathbf{4}\ (79\text{–}87\%)}{R^1R^2\overset{+}{S}NHCOCH_3\ Cl^-}$$

a, $R^1 = R^2 = CH_3$; **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**, $R^1 = R^2 = i\text{-}C_3H_7$; **f**, $R^1,R^2 = -(CH_2)_4-$

The yields and melting points of the iminosulfuranes (**2**), sulfonium bromides (**3**), and sulfonium chlorides (**4**) are given in Table I.

N-Bromoacetamide (NBA) is a source of positive bromine and is an oxidizing agent in aqueous media. Consequently, a thoroughly dry and inert solvent system is required for the preparation of the sulfonium bromides (**3**). In carbon tetrachloride, the reaction of NBA with sulfides is slow and in ether the major product is acetamide hydrobromide, $(CH_3CONH_2)_2HBr$. Chloroform and ethyl alcohol are also unsatisfactory solvents because of the predominance of substitution and oxidation reactions. The best solvent system found for the reaction is a mixture of carbon tetrachloride and acetone (4–8:1 by volume); under these conditions the reaction mixture is heterogeneous. The sulfonium bromides (**3**) precipitate at the reaction temperature (0°).

The sulfonium bromides (**3**) are white, crystalline

(1) (a) For part III, see H. Kise, G. F. Whitfield, and D. Swern, *Tetrahedron Lett.*, 1761 (1971). (b) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Apr 1971. (c) Postdoctoral Fellow from the University of Tokyo. (d) Postdoctoral Fellow from the University of London.

(2) B. Cohen and A. G. MacDiarmid, *Angew. Chem.*, **75**, 207 (1963).

(3) P. Claus and W. Vycudilik, *Tetrahedron Lett.*, 3607 (1968).

(4) K. Seppelt and W. Sundermeyer, *Angew. Chem., Int. Ed. Engl.*, **8**, 771 (1969).

(5) F. D. Marsh, U. S. Patent 3,505,401 (1970); *Chem. Abstr.*, **72**, 132102f (1970).

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

(7) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

(8) J. Sauer and K. K. Mayer, *Tetrahedron Lett.*, 319 (1968).

(9) D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, **63**, 2939 (1941).

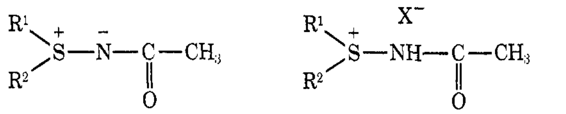
(10) R. Neidlein and E. Heukelbach, *Arch. Pharm. (Weinheim)*, **299**, 64 (1966).

(11) A. Kucsman, F. Ruff, I. Kapovits, and J. G. Fischer, *Tetrahedron*, **22**, 1843 (1966).

(12) M. V. Likhosherstov, *Zh. Obshch. Khim.*, **17**, 1478 (1947).

TABLE I

N-ACETYLIMINODIALKYLSULFURANES AND THEIR SALTS[b]



2

3, X = Br
4, X = Cl

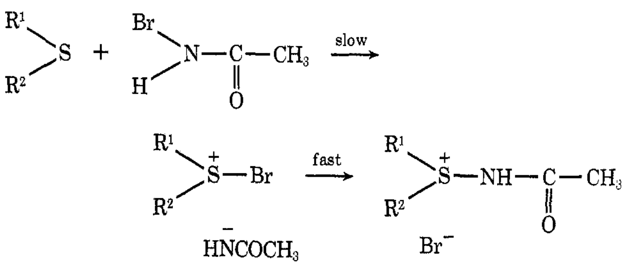
R^1	R^2	Compd	Yield, %	Mp, °C
CH_3	CH_3	**2a**	88	67–68
		3a	81	111–112 dec
		4a	79	132–133 dec[a]
CH_3	C_2H_5	**2b**	94	59–60
		3b	66	109–110
C_2H_5	C_2H_5	**2c**	98	<30
		3c	67	110–111 dec
		4c	87	116–117 dec
n-C_3H_7	*n*-C_3H_7	**2d**	95	36–38
		3d	38	86–88
i-C_3H_7	*i*-C_3H_7	**2e**	95	<30
		3e	52	124–125 dec
–$(CH_2)_4$–		**2f**	95	66–68
		3f	72	115–117 dec

[a] Lit.[12] mp 78–90°. [b] Satisfactory analyses (±0.4%) for C, H, N, and S were obtained for all new compounds listed. Ed.

solids that can be recrystallized from alcohol or mixtures of alcohol and ether without decomposition. They are stable in water at room temperature.

A suggested pathway for the reaction of NBA with sulfides is given in Scheme II.

SCHEME II



3

Although the work-up conditions were not exactly the same for all the NBA–sulfide reactions, there is some indication that electron-donating groups on sulfur facilitate the reaction, giving the sulfonium bromides (**3**) in higher yields (Table I). This can be explained by assuming that the rate-determining step is the first one in Scheme II. A similar mechanism was proposed for the reaction of sulfides with chloramine-T to give *N*-tosyliminosulfuranes.[13]

Reaction of NBA with di-*tert*-butyl sulfide failed to yield the sulfonium bromide, presumably due to steric hindrance by the *tert*-butyl groups. Furthermore, we have been unable, to date, to prepare sulfonium bromides (**3**) *via* the reaction of NBA with methyl phenyl sulfide and diphenyl sulfide.

N-Acetyliminodialkylsulfuranes (**2**) were obtained by treatment of the sulfonium bromides (**3**) with triethylamine in methylene chloride at 0°. The purity of **2** was supported by mass spectrometry, nmr, and microanalysis. The iminosulfuranes (**2**) are oils or delinquescent, crystalline solids. They decompose in water at room temperature within a few days to acetamide and the corresponding sulfoxide, except **2e** ($R^1 = R^2 = i\text{-}C_3H_7$), which is stable in water at room temperature for more than 10 days.

Treatment of iminosulfuranes **2a** and **2c** with hydrogen bromide or hydrogen chloride gave the sulfonium bromides (**3a** and **3c**) or chlorides (**4a** and **4c**), respectively. The sulfonium chlorides are stable in water and they can be recrystallized from alcohol without decomposition, contrary to the statement by Likhosherstov[12] who reported that **4a** rapidly decomposes on exposure to moisture.

Spectral Characteristics.[14]—*N*-Acetyliminosulfuranes **2** show some variation in the position of the S–N and C=O stretching bands with change of R^1 and R^2. The greatest differences are found in iminosulfuranes **2e** and **2f**; the former has the highest C=O (1600 cm^{-1}) and the second highest S–N frequencies (802 cm^{-1}), whereas the latter has the lowest (1540 and 788 cm^{-1}). The nmr resonance of the β-methyl protons in **2e** appears as a doublet of doublets, while in the salt **3e** it appears as a doublet. In addition, **2e** is stable in water at room temperature in contrast to **2f**, which decomposes quite rapidly.

The observation of a doublet of doublets for the methyl groups of **2e** in the nmr clearly demonstrates their magnetic nonequivalence. The reason for this is not clear. However, the higher S–N frequency observed in **2e** suggests partial double bond character (S=N) and this, coupled with the greater bulk of the isopropyl groups, could give rise to restricted rotation about the S–N bond, resulting in two sets of nonequivalent methyl groups. The steric effect appears to be more important because in other ylides (**2c**, **2d**) the β protons are identical even though the ir spectra suggest similar S–N double bond character.

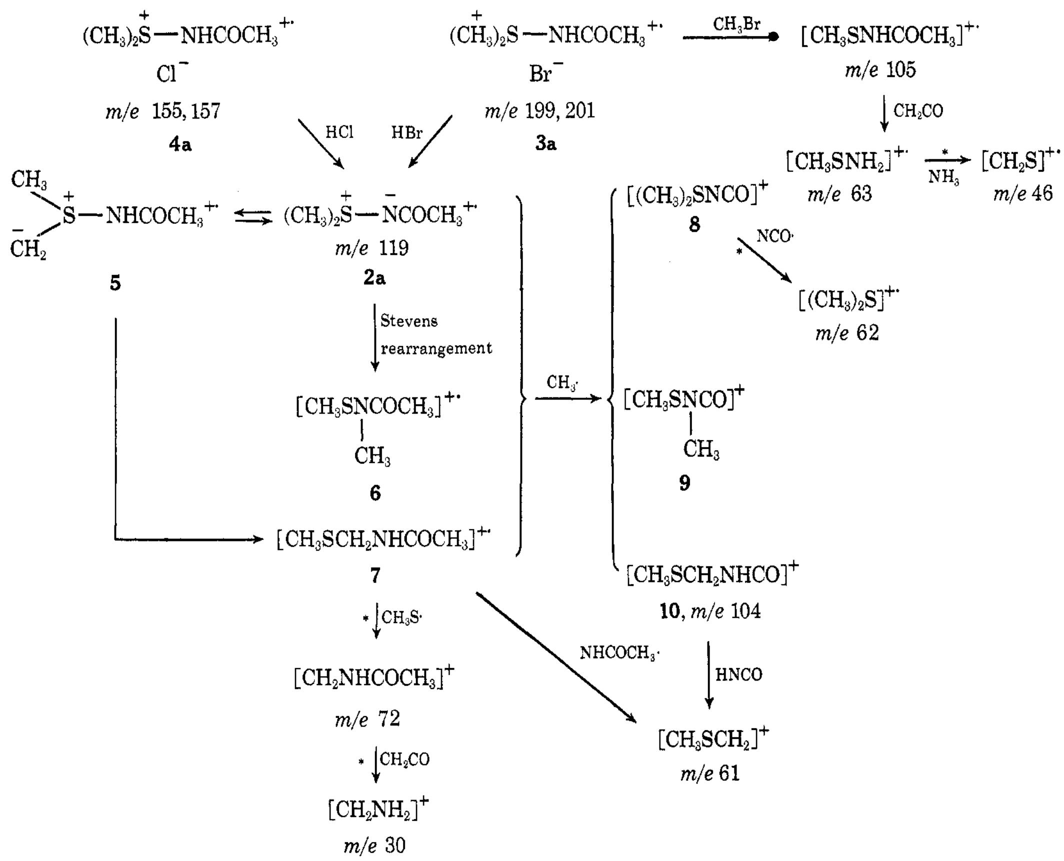
In the uv spectra of iminosulfuranes **2a** and **2c**, large differences were noted between λ_{max} in alcohol and chloroform; these are too large to be accounted for as an ordinary solvent effect. Also, the absorption did not follow the Beer–Lambert law; ϵ decreased with increasing concentration.

Mass Spectrometry.[14]—The literature on mass spectral fragmentations of ylides is sparse; our detailed study of the mass spectra of iminosulfuranes is the first report of their fragmentation pathways. The high-resolution mass spectra of the iminosulfuranes **2a** and **2c** and of their salts (**3a**, **4a**, **3c**, and **4c**) were obtained (see Experimental Section). A condensed "superimposed" version of the spectra of **2a**, **3a**, and **4a** is shown in Scheme III. The mass spectral fragmentations of **2a** and **4a** are quite similar. The primary fragmentation of **4a** is loss of HCl to give **2a**. The sulfonium bromide **3a** also loses HBr to give **2a**, but, in this case, loss of methyl bromide is another primary fragmentation pathway. The subsequent fragmentations of **2a** indicate that some kind of rearrangement

(13) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc., Jap.*, **42**, 2631 (1969).

(14) Some spectral data on 6 of the 14 compounds described in this paper have been reported in the preliminary communication.[1a] The remaining ir, nmr, and uv data, as well as mass spectral bar graphs for compounds **2a** and **2c** (Table I), will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-1121. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

SCHEME III



is involved. The formation of the ion at *m/e* 104 can occur in several ways: (1) loss of $CH_3\cdot$ directly from **2a** to give structure **8**; (2) Stevens rearrangement of **2a** to give **6** followed by loss of $CH_3\cdot$ affording **9**; (3) formation of the ylide **5** by a 1,3-prototropic shift, followed by a Stevens rearrangement and loss of $CH_3\cdot$ to give **10**.

The genesis of the fragment at *m/e* 72 involves loss of $CH_3S\cdot$ from the ion at *m/e* 119, and either of the two structures shown (**6** or **7**) appears to be equally feasible. However, the elimination of ketene from *m/e* 72 to give the ion at *m/e* 30 and the formation of the ion at *m/e* 61 (C_2H_5S) suggest that structure **7** is more likely.

Another interesting fragmentation is the loss of methyl bromide from the molecular ion of **3a** to give the fragment at *m/e* 105. This is not observed in the sulfonium chloride **4a** and, accordingly, it appears that the nature of the anion in sulfonium salts has some influence on the primary fragmentation mode.

A condensed version of the spectra of **2c**, **3c**, and **4c** is shown in Scheme IV. As with the analogous dimethyl compounds described above, the primary fragmentation of **4c** is loss of HCl to give **2c**, whereas **3c** loses either HBr or ethyl bromide to afford **2c** or *N*-(ethylthio)acetamide (**15**) (*m/e* 119). Elimination of C_2H_4 from **2c** also gives **15**, which then cleaves in two ways: (a) loss of ketene affords an abundant ion at *m/e* 77, which then loses C_2H_4 giving the fragment at *m/e* 49; and (b) elimination of $CH_3\cdot$ yields the ion at *m/e* 104, which then loses HNCO and CO in two distinct metastable processes to give the fragments at *m/e* 61 and 76, respectively. It seems likely that a 1,3-prototropic shift converts the iminosulfurane (sulfilimine) ion radical (Scheme IV) into the ylide ion radical (**11**), which then undergoes a Stevens type rearrangement affording the fragment of structure **12**. Loss of $C_2H_5S\cdot$ from **12** yields the ion at *m/e* 86 (metastable peak observed); the formation of the ion at *m/e* 89 is additional evidence for structure **12**.

Experimental Section

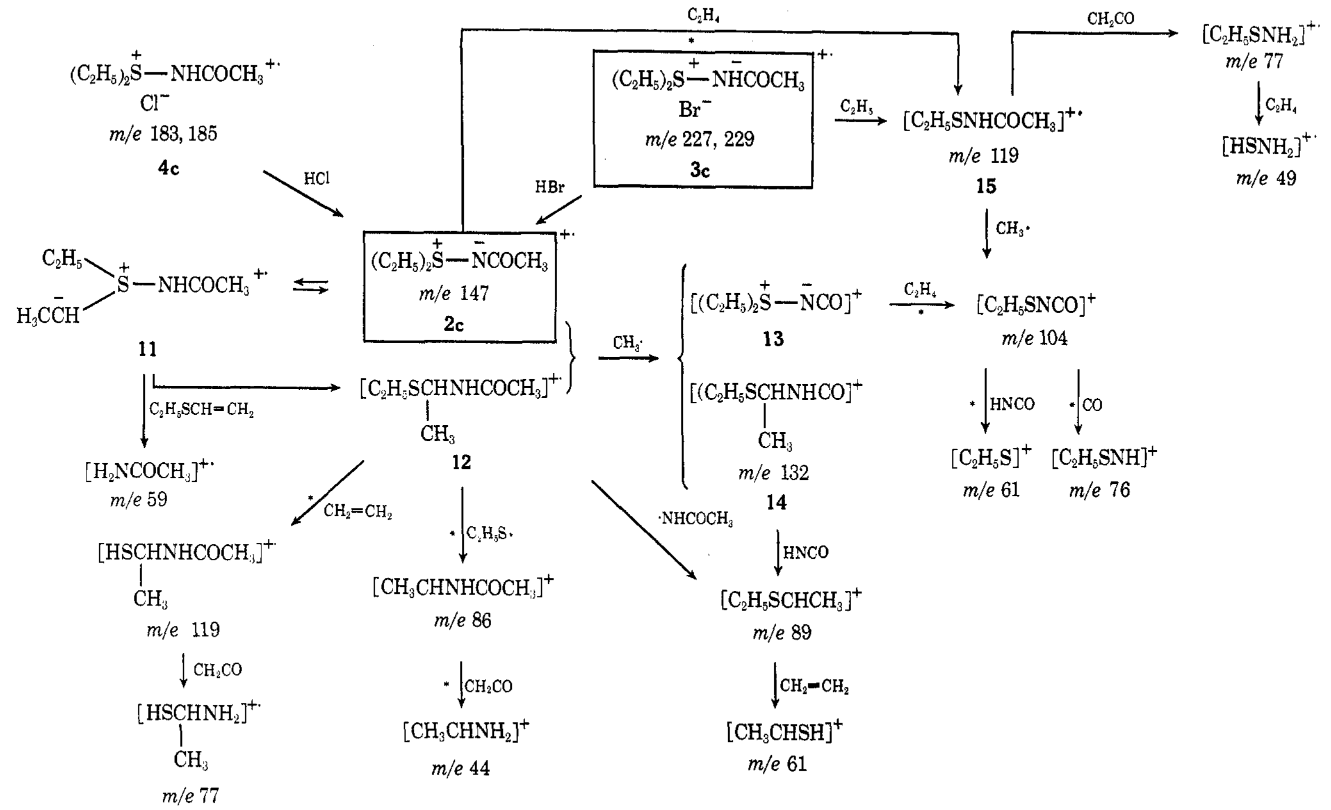
Ir, Nmr, and Uv.—Ir spectra were obtained as KBr discs or liquid films using a Perkin-Elmer Model 225 grating ir spectrophotometer or an Infracord spectrophotometer Model 137B. Nmr spectra of salts and iminosulfuranes were obtained with a Varian A-60A spectrometer, using D_2O as solvent and DSS (sodium 2,2-dimethyl-2-silapentanesulfonate) as internal standard. Nmr spectra of the iminosulfuranes **2** were also taken in $CDCl_3$ using TMS as internal standard. The differences in chemical shift in the two solvents were within 0.1 ppm except for the methine protons in **2e**, in which the difference was 0.18 ppm. When **2** has methylene groups attached to sulfur, they appear as ABX_n type spectra giving multiplets for **2b**, **2c**, **2d**, and **2f**. Uv spectra were obtained with a Perkin-Elmer spectrometer Model 202.

Preparation of *N*-Acetyliminodimethylsulfonium Bromide (3a).—A solution of dimethyl sulfide (20.3 g, 0.327 mol) in dry CCl_4 (80 ml) was added dropwise with stirring to a supension of *N*-bromoacetamide (32.0 g, 0.232 mol) in a mixture of CCl_4 (160 ml) and dry acetone (60 ml) at 0° over 1 hr. The reaction was exothermic; after 5 hr the precipitate was separated, washed with cold acetone, and dried under vacuum at room temperature. Recrystallization from EtOH gave pure **3a** (37.4 g, 81% yield), mp 111–112° dec.

The other sulfonium bromides (**3b–f**) were prepared similarly using smaller amounts of acetone (30–45 ml) and a longer reaction time for **3d** and **3e** (30 hr). Yields and melting points of **3** are shown in Table I.

Preparation of *N*-Acetyliminodimethylsulfurane (2a).—Freshly distilled triethylamine (17.0 g, 0.168 mol) was added dropwise with stirring to a supension of **3a** (30.7 g, 0.154 mol) in dry CH_2Cl_2 (200 ml) at 0° over 20 min. After 1 hr, the reaction mixture was concentrated to about 100 ml and ether (200 ml) was added at

SCHEME IV



0°. The precipitate ($Et_3N \cdot HBr$) was separated by filtration and washed with cold ether (27.5 g, yield 98%). The solvents were removed from the filtrate at room temperature (rotary evaporator, water pump pressure) and the residue was then dried under vacuum at room temperature for 2 hr. A colorless, crystalline solid was obtained ; it was found to be pure **2a** (16.2 g, 88% yield), mp 67–68°. The purity of **2a** was established by microanalysis and nmr and mass spectral measurements.

The other iminosulfuranes (**2b–f**) were prepared similarly. Yields and melting points of **2** are shown in Table I.[14]

The stability of **2** in water was examined by nmr; in the case of **2a**, the formation of dimethyl sulfoxide and acetamide was confirmed.

Preparation of *N*-Acetyliminodimethylsulfonium Chloride (4a).—Aqueous HCl (37%, 0.44 ml, 0.0053 mol HCl) was added dropwise with stirring to a solution of **2a** (0.53 g, 0.0044 mol) in acetone (7 ml) at 0°. After 2 hr, the precipitate was separated, washed with cold acetone, and dried under vacuum. Pure sulfonium chloride **4a** was obtained by recrystallization from EtOH–Et_2O (0.55 g, 79%), mp 132–133° dec.

The analogous diethylsulfonium chloride (**4c**) was obtained by using dry HCl instead of aqueous HCl, and ether instead of acetone. Yields and melting points are shown in Table I.[14]

Mass Spectrometry.—The spectra were run using an A.E.I. MS 902 instrument, at 70 eV, ion source temperature 200°. The sample was introduced (a) *via* direct insertion probe for **3a** (100°), **4a** (100°), **2c** (130°), **3c** (100°), and **4c** (130°); (b) *via* heated inlet for **2a** (200°). The data are presented using the following format: *m/e* value (rel abundance), fragment assignment, molecular formula (difference between the calculated and observed masses). Results with **2a**: *m/e* 119 (29), molecular ion, C_4H_9NOS (4.7 ppm); 104 (100), M − $CH_3\cdot$, C_3H_6NOS (6.0 ppm); 89 (12), *m/e* 104 − $CH_3\cdot$, C_2H_3NOS (11.4 ppm); 72 (23), *m/e* 119 − $CH_3S\cdot$, C_3H_6NO (3.7 ppm); 62 (67), *m/e* 104 − $NCO\cdot$, C_2H_6S (33.7 ppm); 62 (30), *m/e* 104 − ketene, CH_4NS (33.1 ppm); 61 (18), *m/e* 104 − HNCO and *m/e* 119 − $NHCOCH_3\cdot$, C_2H_5S (40.9 ppm); 47 (28), CH_3S (34.8 ppm); 46 (13), *m/e* 62 − CH_4, CH_2S (26.5 ppm); 45 (13), CHS (34.3 ppm); 43 (22), CH_3CO (45.8 ppm); 41 (18), *m/e* 72 − CH_3O, C_2H_3N (41.0 ppm); 30 (5), *m/e* 72 − ketene, CH_4N (18.4 ppm).

Results with **3a**: *m/e* 119 (12), M − HBr, C_4H_9NOS (2.3 ppm); 105 (21), M − CH_3Br, C_3H_7NOS (5.3 ppm); 104 (41), *m/e* 119 − CH_3, C_3H_6NOS (4.3 ppm); 96 (54), $CH_3{}^{81}Br$ (1.9 ppm); 94 (59), $CH_3{}^{79}Br$ (8.7 ppm); 89 (4), *m/e* 104 − CH_3, C_2H_3NOS (2.7 ppm); 82 (16), $H^{81}Br$ (3.0 ppm); 80 (17), $H^{79}Br$ (5.4 ppm); 72 (10), *m/e* 119 − CH_3S, C_3H_6NO (4.1 ppm); 63 (100), *m/e* 105 − ketene, CH_5NS (3.3 ppm); 62 (25), *m/e* 104 − NCO, C_2H_6S (4.8 ppm); 62 (21), *m/e* 104 − ketene, CH_4NS (8.0 ppm); 61 (7), *m/e* 104 − HNCO and *m/e* 119 − $NHCOCH_3$, C_2H_5S (9.9 ppm); 59 (34), *m/e* 105 − CH_2S, C_2H_5NO (4.4 ppm); 47 (23), CH_3S (16.0 ppm); 46 (14), *m/e* 63 − NH_3 and *m/e* 62 − CH_4, CH_2S (27.4 ppm); 45 (16), *m/e* 62 − NH_3, CHS (27.8 ppm); 44 (24), *m/e* 59 − CH_3, CH_2NO (30.6 ppm); 43 (77), $COCH_3$ (35.1 ppm); 41 (11), *m/e* 72 − OCH_3, C_2H_3N (34.5 ppm).

Results with **4a**: *m/e* 119 (40), M − HCl, C_4H_9NOS (0.5 ppm); 104 (100), M − [HCl + $CH_3\cdot$], C_3H_6NOS (23.6 ppm); 89 (12), *m/e* 104 − $CH_3\cdot$, C_2H_3NOS (20.5 ppm); 77 (7), *m/e* 119 − ketene, C_2H_7NS (13.2 ppm); 76 (4), *m/e* 119 − $CH_3CO\cdot$, C_2H_6NS (9.5 ppm); 72 (33), *m/e* 119 − $CH_3S\cdot$, C_3H_6NO (22.4 ppm); 62 (67) *m/e* 104 − $NCO\cdot$, C_2H_6S (61.3 ppm); 62 (35), *m/e* 104 − ketene, CH_4NS (54.9 ppm); 61 (23), *m/e* 104 − HNCO and *m/e* 119 − $NHCOCH_3$, C_2H_5S (18.6 ppm); 60 (5), *m/e* 119 − $C_2H_3S\cdot$, C_2H_6NO (20.4 ppm); 59 (1), C_2H_3S (37.8 ppm); 47 (24), CH_3S (25.3 ppm); 43 (30), CH_3CO (37.9 ppm); 30 (unknown), *m/e* 62 − S, *m/e* 72 − ketene, and *m/e* 77 − $CH_3S\cdot$, CH_4N.

Results with **2c**: *m/e* 147 (16), molecular ion, $C_6H_{13}NOS$ (3.2 ppm); 132 (50), M − CH_3, $C_5H_{10}NOS$ (4.6 ppm); 119 (18), M − C_2H_4, C_4H_9NOS (6.6 ppm); 104 (23), *m/e* 119 − CH_3, C_3H_6NOS (4.9 ppm); 90 (20), *m/e* 132 − NCO, $C_4H_{10}S$ (0.7 ppm); 89 (53), *m/e* 147 − $NHCOCH_3$ and *m/e* 132 − HNCO, C_4H_9S (5.1 ppm); 86 (26), *m/e* 147 − EtS, C_4H_8NO (4.9 ppm); 77 (90), *m/e* 119 − ketene, C_2H_7NS (2.3 ppm); 76 (34), *m/e* 104 − CO, C_2H_6NS (9.5 ppm); 76 (14), *m/e* 104 − C_2H_4, CH_2NOS (4.2 ppm); 75 (24), *m/e* 90 − CH_3, C_3H_7S (1.4 ppm); 62 (20), *m/e* 104 − NCO and *m/e* 90 − C_2H_4, C_2H_6S (10.6 ppm); 62 (18), *m/e* 104 − ketene, CH_4NS (2.9 ppm); 61 (86), *m/e* 104 − HNCO and *m/e* 89 − C_2H_4, C_2H_5S (6.9 ppm); 60 (17), *m/e* 77 − NH_3, C_2H_4S (1.8 ppm); 60 (74), *m/e* 86 − C_2H_2, C_2H_6NO (12.5 ppm); 59 (4), *m/e* 119 − C_2H_4S and *m/e* 147 − C_4H_8S, C_2H_5NO (8.8 ppm); 49 (50), *m/e* 77 − C_2H_4, H_3NS (7.7 ppm); 48 (17), *m/e* 76 − CO and *m/e* 76 − C_2H_4, H_2NS (2.0 ppm); 47 (14), *m/e* 62 − CH_3, CH_3S (5.1 ppm); 45 (10), *m/e* 62 − NH_3 and *m/e* 60 − CH_3, CHS (25.9 ppm); 44 (2), *m/e* 86 − ketene, C_2H_6N (10.1 ppm); 43 (100), *m/e* 119 − EtSNH, CH_3CO (23.7 ppm); 41 (45), C_2H_3N (39.3 ppm); 29 (49), C_2H_5 (26.0 ppm); 28 (85) C_2H_4 (36.2 ppm).

Results with **3c**: *m/e* 147 (3), M − HBr, $C_6H_{13}NOS$ (21.1

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 − $NHCOCH_3$· 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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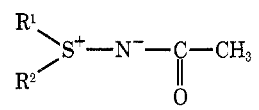
The thermolysis of N-acetyliminodialkylsulfuranes, $R^1R^2S^+N^-COCH_3$ ($R^1 = CH_3$, $R^2 = C_2H_5$; $R^1 = R^2 = C_2H_5$; $R^1 = R^2 = n\text{-}C_3H_7$; $R^1 = R^2 = i\text{-}C_3H_7$), in xylene affords olefin (ethylene or propylene) and N-(alkylthio)acetamides, $RSNHCOCH_3$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$), 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.



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, $R^1 = R^2 = i\text{-}C_3H_7$

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.

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).