2-*t*-Butylmercapto-3-picoline (43.5%, rt 59.8 min): pmr ($CDCl_3$) δ 8.07 (H-6), 7.05 (H-4), 6.63 (H-5) ($J_{4,5}$ = 7.1, $J_{4,6}$ = 1.8, $J_{5,6}$ = 4.7 Hz), 2.18 (CH_3), 1.53 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.57, H, 8.44; N, 7.57.

2-*t*-Butylmercapto-5-picoline (17.9%, rt 63.4 min): pmr ($CDCl_3$) δ 8.10 (H-6), 7.10 (H-3, H-4, br m), 2.22 (CH_3), 1.40 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.78; H, 8.46; N, 7.69.

3-*t*-Butylmercapto-5-picoline (34.8%, rt 67.0 min): pmr ($CDCl_3$) δ 8.22, 8.13 (H-2, H-6), 7.42 (H-4) ($J_{2,4}$ = $J_{4,6}$ = 1.3 Hz), 2.27 (CH_3), 1.25 (*t*-C_4H_9). *Anal.* Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73. Found: C, 66.20; H, 8.54; N, 7.69.

I. 3,5-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 3,5-lutidine 1-oxide (0.1 mol) as described under A provided an oil (12.8 g) of bp 56–58° (0.1 mm). Gc[37] examination of this oil revealed only one component which was **2-*t*-butylmercapto-3,5-lutidine**: pmr ($CDCl_3$) δ 8.08 (H-6), 7.07 (H-4) ($J_{4,6}$ = 2.0 Hz), 2.20, 2.17 (CH_3), 1.53 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.79; H, 8.66; N, 7.01.

J. 3,4-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction when carried out with 3,4-lutidine 1-oxide (0.1 mol) as described under A provided an oil (9.0 g) of bp 90–91° (0.1 mm) which was separated by gc[37] (injection temperature 150°) and found to contain the following components.

(3-Methyl-4-pyridine)methyl acetate (21.5%, rt 44.5 min): pmr ($CDCl_3$) δ 8.30 (H-2), 8.10 (H-6), 7.17 (H-5), 5.05 (4-CH_2O), 2.27 (3-CH_3), 2.13 (CH_3CO_2).

2-*t*-Butylmercapto-3,4-lutidine (36.2%, rt 56.8 min): pmr ($CDCl_3$) δ 7.90 (H-6), 6.55 (H-5) ($J_{5,6}$ = 4.5 Hz), 2.13 (CH_3), 1.50 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.69; H, 8.77; N, 7.29.

2-*t*-Butylmercapto-4,5-lutidine (17.3%, rt 60.4 min): pmr ($CDCl_3$) δ 8.00 (H-6), 6.95 (H-3), 2.13 (CH_3), 1.40 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.45; H, 8.73; N, 7.21.

3-*t*-Butylmercapto-4,5-lutidine (21.7%, rt 64.8 min): pmr ($CDCl_3$) δ 8.30, 8.05 (H-2, H-6), 2.40, 2.20 (CH_3), 1.23 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.59; H, 8.86; N, 6.94.

4-(*t*-Butylmercapto)methyl-3-picoline (3.3%, rt 67.2 min): pmr ($CDCl_3$) δ 8.12 (H-2, H-6), 6.98 (H-5), 3.88 (CH_2), 2.30 (CH_3), 1.33 (*t*-C_4H_9). *Anal.* Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.17. Found: C, 67.68; H, 8.68; N, 7.20.

Based on the N-oxide, the total yield of sulfides was 36% and that of pyridyl esters was 11%.

K. 2,6-Lutidine 1-Oxide with *t*-Butyl Mercaptan.—The reaction was carried out with 2,6-lutidine 1-oxide (0.1 mol) as described under A and yielded an oil (8.2 g) of bp 75–78° (0.1 mm) which was separated by gc[37] (injection temperature 110°) and found to contain the following components.

3-(2,6-Dimethyl)pyridyl acetate (29.5%, rt 39.0 min): pmr ($CDCl_3$) δ 7.10 (H-3, H-4, center of AB quartet), 2.50, 2.40 (2-CH_3, 6-CH_3), 2.30 (CH_3CO_2).

(6-Methyl-2-pyridine)methyl acetate (65.6%, rt 43.6 min): pmr ($CDCl_3$) δ 6.92–7.67 (H-3, H-4, H-5), 5.15 (2-CH_2O), 2.50 (6-CH_3), 2.08 (CH_3CO_2).

2-(*t*-Butylmercapto)methyl-6-picoline (3.0%, rt 55.8 min): pmr ($CDCl_3$) δ 7.15, 6.88 (H-3, H-5), 7.43 (H-4) ($J_{3,4}$ = $J_{4,5}$ = 7.5, $J_{3,5}$ = 1.4 Hz), 3.83 (CH_2), 2.43 (CH_3), 1.27 (*t*-C_4H_9); ir spectrum identical with that of an authentic sample, whose preparation is described above.

Based on the starting N-oxide, the total yield of lutidyl sulfides was 1% and of lutidyl acetates was 47%.

Registry No.—4-*t*-Butylmercaptopyridine, 18794-26-8; 4-picolyl *t*-butyl sulfide, 18794-27-9; 2-(*t*-butylmercapto)methyl-6-picoline, 18794-28-0; 2-*t*-butylmercaptopyridine, 18794-29-1; 3-*t*-butylmercaptopyridine, 18794-30-4; 3-pyridyl acetate, 17747-43-2; 2-methylmercaptopyridine, 18434-38-5; 3-methylmercaptopyridine, 18794-33-7; 3-acetoxy-4-picoline, 1006-96-8; 4-picolyl acetate, 1007-48-3; 2-*t*-butylmercapto-4-picoline, 18794-36-0; 3-*t*-butylmercapto-4-picoline, 18794-37-1; 2-*t*-butylmercapto-4-*t*-butylpyridine, 18794-38-2; 3-*t*-butylmercapto-4-*t*-butylpyridine, 18794-39-3; 3-*t*-butylmercapto-4-phenylpyridine, 18794-40-6; 2-*t*-butylmercapto-4-phenylpyridine, 18794-41-7; 2-picolyl acetate, 1007-49-4; 6-*t*-butylmercapto-2-picoline, 18794-43-9; 5-*t*-butylmercapto-2-picoline, 18794-44-0; 2-picolyl *t*-butyl sulfide, 18794-45-1; 2-*t*-butylmercapto-3-picoline, 18833-87-9; 2-*t*-butylmercapto-5-picoline, 18794-46-2; 3-*t*-butylmercapto-5-picoline, 18794-47-3; 2-*t*-butylmercapto-3,5-lutidine, 18794-48-4; (3-methyl-4-pyridine)methyl acetate, 18794-49-5; 2-*t*-butylmercapto-3,4-lutidine, 18794-50-8; 2-*t*-butylmercapto-4,5-lutidine, 18794-51-9; 3-*t*-butylmercapto-4,5-lutidine, 18794-52-0; 4-(*t*-butylmercapto)methyl-3-picoline, 18794-53-1; 3-(2,6-dimethyl)pyridyl acetate, 18794-54-2; (6-methyl-2-pyridine)methyl acetate, 13287-64-4; 2-(*t*-butylmercapto)methyl-6-picoline, 18794-28-0; acetic anhydride, 108-24-7.

The Chemistry of Pyridine. VII. Tetrahydropyridines from the Reaction of Pyridine N-Oxides with Mercaptans in Acetic Anhydride

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Received August 2, 1968

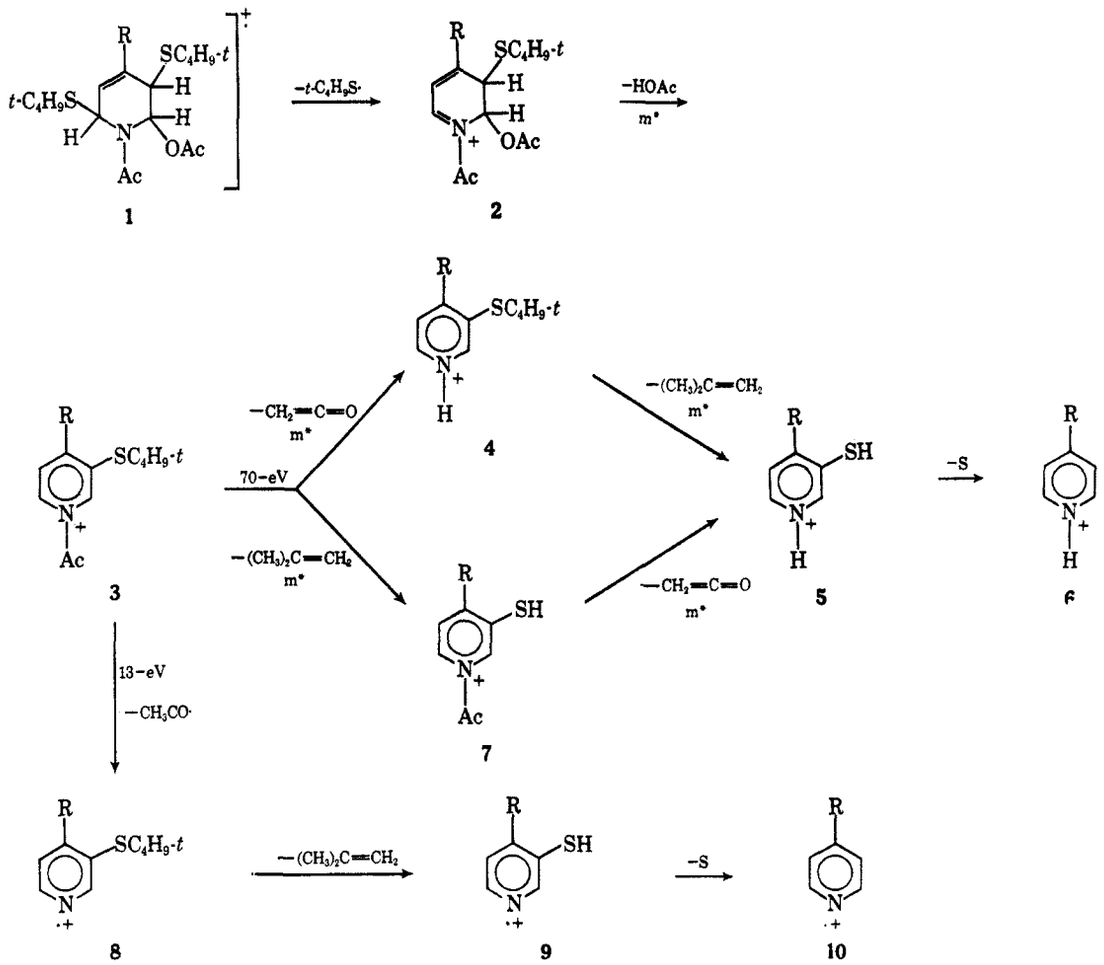
A number of solids isolated from the reaction of pyridine N-oxides with mercaptans in acetic anhydride were shown to be 1-acetyl-1,2,3,6-tetrahydropyridines. One feature common to these compounds was that a sulfide group was attached to the β sp^3 ring carbon while both the α positions on the ring were substituted by either sulfide or acetoxy groups. The formation of these products is discussed in terms of the episulfonium intermediate proposed in the prior paper.[2]

Structure proofs are presented for a number of crystalline high molecular weight by-products isolated from the reaction of the N-oxides of pyridine, 4-picoline, 4-*t*-butylpyridine, 4-phenylpyridine, and 3,5-lutidine with *t*-butyl mercaptan in acetic anhydride.[2] A similar product was obtained from pyridine 1-oxide, methyl mercaptan, and acetic anhydride.[2] Spectral data confirm these compounds to be the tetrahydropyridines, **1a–d** and **11–13** (CH_3CO abbreviated to Ac throughout). In these piperideines, alkyl or aryl groups

(1) National Science Foundation Trainee. Abstracted from the Ph.D. Dissertation of F. M. H., University of Illinois at the Medical Center, Chicago, Ill., June 1968.

(2) F. M. Hershenson and L. Bauer, *J. Org. Chem.*, **34**, 655 (1969).

SCHEME I



a, R = H; b, R = CH_3; c, R = C_6H_5; d, R = C_4H_9-*t*

occupied the same ring positions as in the original N-oxide.

Proton Magnetic Resonance (Pmr) Spectra.—Although these spectra in various solvents, at ambient or elevated temperatures, proved to be relatively complex,[3] they attested to the aliphatic nature of these molecules. The multiplets furthest downfield between δ 5.0 and 6.7 indicated the presence of only alkene and possibly highly deshielded methine protons. The upfield signals, δ 1.0–2.4, were assigned to the various methyl groups present in these compounds. The absence of exchangeable protons and discrete signals between δ 1.0 and 4.5 attributable to methylene groups was consistent with the proposed structures.

Infrared (Ir) Spectra in CCl_4.—The lack of absorption above 3100 cm^{-1} established the absence of OH and NH groups in these piperideines. The presence of one strong band between 1665–1690 cm^{-1} is attributed to $\nu_{C=O}$ of a tertiary amide although this absorption could be due to $\nu_{C=C}$, of a system $-C{=}C\dot{X}R$, *e.g.*, in an enamide ($\dot{X}R$ being NAc) or enol acetate.[4,5] Except for **12**, all other products showed strong absorption between 1745 and 1760 ($\nu_{C=O}$) and around 1230 cm^{-1} (ν_{C-O-C}) characteristic of acetates.[4]

Ultraviolet (Uv) Spectra.—Uv absorption pinpointed the double bond in these piperideines to be β,γ to the ring nitrogen atom. The single maximum at 200 ± 5 mμ in hexane or methanol (ϵ ~10,000) is consistent with the 1-acetyl-1,2,3,6-tetrahydropyridine assignment.[6] The product, **1c**, from 4-phenylpyridine 1-oxide showed an additional band around 248 mμ which was to be expected if the arene was conjugated with the alkene.[7]

Mass Spectra.[8]—Electron-impact-induced decompositions of four of the piperideines (**1a–d**) were so closely related that their relevant fragmentations can be summarized in Scheme I. Hence, this discussion involves only the salient features of the mass spectrum of the product from pyridine 1-oxide, *t*-butyl mercaptan, and

(3) R. S. Egan, F. M. Hershenson, and L. Bauer, *ibid.*, **34**, 665 (1969).

(4) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(5) For 1-acetyl-1,2,3,6-tetrahydropyridine, $\nu_{C=C}$ and $\nu_{C=O}$ were reported at 1660 and 1630 cm^{-1}, respectively [F. Morlacchi, M. Cardellini, and F. Liberatore, *Ann. Chim.* (Rome), **57**, 1456 (1967)].

(6) The isolated alkene in 1,2,3,6-tetrahydropyridine absorbed at lower wavelength than a 1,2,3,4 isomer. For example, 1-ethyl-1,2,3,6- and -1,2,3,4-tetrahydropyridines absorbed at 218 mμ (log ϵ 3.23) and 231 mμ (log ϵ 3.71) in ethyl ether [N. J. Leonard and D. M. Locke, *J. Amer. Chem. Soc.*, **77**, 437 (1955)]; 1-acetyl-1,2,5,6- and -1,4,5,6-tetrahydronicotinamides possessed uv maxima at 205 mμ (log ϵ 4.29) and 210, 274 mμ (log ϵ 3.78, 4.30), respectively, in water [D. Taub, C. H. Kuo, and N. L. Wendler, *J. Chem. Soc., C*, 1558 (1967)].

(7) R. E. Lyle and W. E. Krueger [*J. Org. Chem.*, **32**, 3613 (1967)] reported a uv maximum for 1-methyl-3-bromo-4-phenyl-1,2,3,6-tetrahydropyridine hydrobromide (C_2H_5OH) at 243 mμ (log ϵ 4.09).

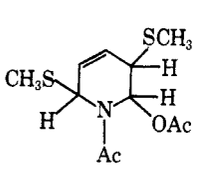
(8) Mass spectra were obtained by Mr. Richard Dvorak using a Hitachi Perkin-Elmer RMU-6D mass spectrometer equipped with a Honeywell Visicorder. Care was exercised to record the spectra at the lowest possible temperature needed to vaporize the sample *via* the direct-inlet system (50–100°). Relative abundances are reported, in general, for fragments over 3% of the base peak, except for M, M + 1. Metastable ions (m*) are reported only for those transitions essential to the arguments.

acetic anhydride **1a**. Pmr data suggested that in **1a** the alkene was unsubstituted and that the ring possessed three additional substituents, *viz.*, one ester and two sulfide groups. Since pyrolysis of **1a** yields 3-*t*-butylmercaptopyridine, one of the sulfide groups of **1a** has to reside on one of the β ring positions and the problem remains to fix the points of attachment of the other sulfide and the ester group to either C-2 or C-6.

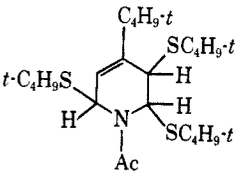
The first major loss from the ion **1a** is that of a *t*-butylmercapto radical, (M − 89), to give rise to an even-electron ion **2a**.[9-11] The subsequent elimination of acetic acid[12] from **2a** to give rise to **3a** is vital since it assigns the acetoxy group in **1a** to C-2 and therefore the remaining sulfide group to C-6. To substantiate that the 1,2 elimination of acetic acid involves H-3, the mass spectrum of the 2,6-d_2 analog of **1a** was examined. The initial loss of 89 was followed by that of 60 (CH_3CO_2H) and not 61 (CH_3CO_2D) which would then arrive at the 2,6-d_2 analog of ion **3a**. At 70 eV, the ion **3a** appears to undergo a series of transformations involving either first the elimination of ketene,[13] then isobutylene,[14] or *vice versa*, leading to **5a**. The remaining fragmentation in Scheme I is the loss of sulfur from **5a** to form the pyridinium ion, **6a**.[15]

The low-voltage spectra (8.5–13 eV) of **1a** suggest that the transitions **1a** → **2a** → **3a** were primary processes, judging from the intensity of these ions. However, the striking difference from the 70-eV spectra was the apparent absence of ions assigned to **4a, 5a,** and **6a.** Instead, up to 13 eV, three ions with 1 mass unit less than **4a, 5a,** and **6a** were quite prominent and it is logical that they are produced from **3a** by successive losses of acetyl radical, isobutylene, and sulfur and are designated by **8a, 9a,** and **10a.** Consecutive increases of voltage on **1a** brought about, first, a greater concentration of the ion **4a,** and to a lesser degree one for **5a** and **6a,** with a noted decrease of ions, **8a, 9a,** and **10a.** From the evidence (see Experimental Section), it appears that **8a** undergoes an ion–molecule interaction to form **4a,** which then decomposes by the pathways suggested in Scheme I. The formation of **4a** from **8a** is probably a competing process with the direct production from **3a.** This could explain why the relative abundances of the four ions **4a** and **8a** and **5a** and **9a,** in particular, varied considerably from run to run.

While the principal electron-impact-induced fragmentation of the four tetrahydropyridines, **1a, 1b, 1c,** and **1d** were quite analogous, there were minor departures from Scheme I for **11,** the product from pyridine 1-oxide, methyl mercaptan, and acetic anhydride. The specific difference is that the loss of



11

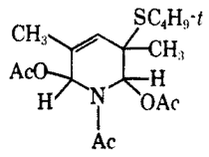


12

isobutylene, so frequently encountered in Scheme I, cannot occur for the fragmentation of **11,** but the ion from **11** (70 eV) loses a methylmercapto radical, acetic acid (m*), ketene (m*), and then a methyl radical to give the odd-electron ion **9** (R = H) which substantiates the proposed structure.

A different problem is posed when, besides **1d,** a second piperideine was isolated from the reaction *t*-butylpyridine 1-oxide with *t*-butyl mercaptan in acetic anhydride. Spectral data point to **12** as being the correct structure. Although the molecular ion is absent in its mass spectrum, that due to the loss of a *t*-butylmercapto radical is present which is quite analogous to process **1a** → **3a.** However, subsequent fragmentations depart from those in Scheme I. Apparently, the analogous 1-acetyl-2,3-dihydropyridinium ion from **12** does not eliminate *t*-butyl mercaptan, but rather loses isobutylene twice (m* observed for both transitions), followed by the expulsion of H_2S which would result in either 1-acetyl- (2- or 3-) mercapto-4-*t*-butylpyridinium ion from which the subsequent loss of ketene (m*) is not unexpected.

The reaction of 3,5-lutidine 1-oxide with *t*-butyl mercaptan in acetic anhydride afforded a solid whose structure is best presented by **13.** The ring substituents in **13** were verified by it pmr spectrum,[3] which also placed the two acetoxy groups on the α carbons (H-2 and H-6 were most deshielded). The fragmentation of



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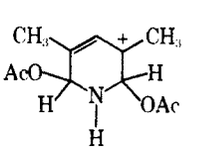

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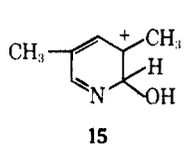
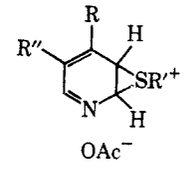


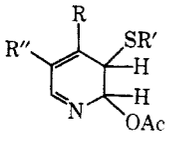
15

13 departed somewhat from that experienced by the other piperideines. Although the initial loss of an α-OAc radical from the molecular ion of **13** is seen as a very weak resultant ion, that of a β-*t*-butylmercapto radical leads to a more prominent ion and also permits explanation of the principal fragmentations. Elimination of ketene (m*) from the latter ion would lead to the symmetrical allyl carbonium ion **14,** which in turn loses acetic acid and ketene (this time from the acetate) to give **15.** To aromatize, **15** loses HO· to arrive at the molecular ion of 3,5-lutidine.

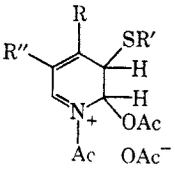
Mechanisms.—An episulfonium salt of type **16,** previously advanced to account for β substitution of pyridine N-oxides,[2] also explains readily the formation of the piperideines under discussion. It would seem



16



17



18

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967.

(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

(11) Although the possibility exists that the sulfide radical departs from C-3 in **1a,** it more likely to take place from C-6 to create **2a** since this follows the well-established α cleavage of cyclic amines (ref 9, p 309; ref 10, p 255).

(12) Studies of electron-impact-induced fragmentation of cyclohexyl acetates have been shown to involve predominantly 1,2 elimination of acetic acid: (a) W. S. Briggs and C. Djerassi, *J. Org. Chem.*, **33,** 1612 (1968), and references quoted therein; (b) ref 9, p 468; (c) M. Venugopalan and C. B. Anderson, *Indian J. Chem.*, **3,** 30 (1965).

(13) Acetamides have been reported to lose ketene on electron bombardment (ref 9, p 338).

(14) It is conceivable that this elimination parallels the one observed for neopentyl phenyl sulfide (ref 9, p 288).

(15) The loss of sulfur has been observed in the fragmentation of the ions of some thionaphthols (ref 9, p 278).

reasonable that, in such a salt in a solvent cage, acetate ion attacks at C-2 to form the 2,3-dihydropyridines **17** initially. It seems that, in acetic anhydride, further reactions take place to provide the more stable tetrahydropyridines. Quaternization of **17** would lead to salts **18**, in which C-6 is quite vulnerable to attack by a nucleophile in the medium, usually the thiol used in the reaction. In two instances, there appears to be some departure from this pattern. To explain the structure of **12**, it would appear that *t*-butyl mercaptan competes with acetate ion to open the ring of **16** (R = R′ = *t*-C_4H_9; R″ = H). It is not unreasonable to assume that in such an intermediate (**16**) ring opening would have to be accomplished in the face of possible steric repulsion between the bulky *t*-butyl group at C-4 and the developing *t*-butyl sulfide group at C-3. Perhaps the enhanced nucleophilicity of the thiol[16] is the driving force to create the logical precursor for **12**. The variation encountered in structure **13**, the product from 3,5-lutidine 1-oxide, is explicable in terms of steric implications. If the 3-methyl analog of **18** is involved (otherwise R = H, R′ = *t*-C_4H_9, and R″ is also CH_3) it is quite conceivable that the bulky *t*-butyl mercaptan might experience difficulty in penetrating between the N-acetyl and β-methyl groups to attach itself at C-6, whereas the smaller acetate ion appears to fit and thus form **13**.

Experimental Section[17]

All experiments described herewith are a continuation of those lettered ones in the Experimental Section of ref 2. To isolate the tetrahydropyridines, the following general work-up was adopted. The original reaction mixture was fractionated *in vacuo*, the distillation of the pyridyl sulfides being conducted under good vacuum, keeping the oil-bath temperature at a minimum to prevent possible thermal decomposition of the high molecular weight products. The viscous residue was dissolved in benzene, chromatographed on alumina (Alcoa, Grade F-20). Petroleum ether refers to that fraction, bp 30–60°.

1-Acetyl-2-acetoxy-3,6-di-*t*-butylmercapto-1,2,3,6-tetrahydropyridine (1a).—The residue which remained after the high-vacuum distillation of the reaction of pyridine 1-oxide (0.3 mol) with *t*-butyl mercaptan in acetic anhydride (expt A[2]) was chromatographed on alumina (300 g). Elution with benzene (1 l.) afforded a yellow gum which solidified and was recrystallized from petroleum ether to furnish a colorless solid (19.35 g, 18%), mp 116–117°, unchanged on further recrystallization from aqueous ethanol; uv max (hexane), 194 mμ (log ε 4.28) (methanol), 204 mμ (log ε 4.28); ir, 1745, 1665 cm^{-1}. *Anal.* Calcd for $C_{17}H_{29}NO_3S_2$: C, 56.78; H, 8.12; N, 3.90; S, 17.82. Found: C, 56.85; H, 8.20; N, 4.01; S, 18.06. Mass spectra were as follows: (70 eV) *m/e* (rel intensity) 359 (3), 271 (2), 270 (14), 211 (2), 210 (14), 180 (4), 169 (6), 168 (29), 167 (16), 154 (9), 138 (9), 132 (14), 122 (4), 113 (6), 112 (38), 111 (62), 110 (5), 96 (11), 90 (10), 84 (4), 83 (5), 80 (24), 79 (21), 78 (7), 75 (8), 67 (7), 60 (8), 59 (7), 58 (5), 57 (100), 56 (13), 55 (10), 53 (7), 52 (14), 51 (10), 50 (9), 49 (4), 45 (13), 43 (49), 42 (6), 41 (62), 40 (5), 39 (34); (13 eV) *m/e* (rel intensity) 361 (4), 360 (6), 359 (33), 302 (10), 272 (10), 271 (20), 270 (100), 211 (6), 210 (39), 180 (8), 169 (12), 168 (12), 167 (60), 138 (4), 135 (16), 132 (30), 122 (4), 113 (4), 112 (6), 111 (77), 99 (6), 90 (37), 79 (24), 57 (30), 56 (33), 43 (4), 41 (6), 32 (4). After the run at 13 eV, additional material was introduced mechanically, *via* the direct inlet system, keeping all other variables constant, particularly temperature. On rerecording the 13-eV spectrum, the intensity of the ion **4a** had increased markedly and, to a lesser extent, that of **5a** compared with those **8a** and **9a**. With a further increase of **1a** in the spectrometer, the intensities of **4a** and **5a** once again increased. At this point, the temperature in the inlet chamber was raised 100°. After a steady state was reached, as judged on the total ion monitor, the spectrum was rerecorded at 13 eV. Once more, the relative abundances of **4a** and **5a** increased, while those of **8a**, **9a** and **10a** decreased. A series of experiments was conducted at constant temperature and concentration but with change of the applied electron voltage. The results are summarized in Table I which lists the total ion current of the pertinent ions.

TABLE I

PER CENT TOTAL ION CURRENT (Σ_{30}) (INLET TEMPERATURE 50°) OF SELECTED IONS FROM **1a**

	Ionizing voltage, eV		
Ions in Scheme I	13	20	70
3a	6.54	5.73	1.91
4a	1.96	5.59	4.05
8a	9.85	4.79	2.45
5a	0.98	3.19	5.43
9a	12.7	15.2	8.67
6a	<0.01	0.53	3.38
10a	3.93	4.79	2.92

A solution of **1a** was stable in acetic anhydride at 120° for 1 hr (pmr spectrum did not change) which indicated that no conversion to 3-*t*-butylmercaptopyridine took place. Exposure of **1a** to acid caused the immediate evolution of *t*-butyl mercaptan and attempts to isolate identifiable materials from the residues from a number of experiments were abortive.

Pyrolysis of **1a** (1 g) at 185° for 0.25 hr gave a liquid (0.3 g, 65%), bp 45° (0.1 mm), whose spectra were identical with that of 3-*t*-butylmercaptopyridine.[2]

Pyridine 1-Oxide-2,6-d_2.—Kawazoe and his co-workers[18a] asserted that H–D exchange of the 2 and 6 protons of pyridine 1-oxide could be effected by D_2O at 180° for 3 hr. In repeating this experiment, a mixture of starting material and pyridine 1-oxides-2-*d* and -2,6-d_2 were isolated (mass spectrum). Attempts to use base catalysis, *e.g.*, 5% NaOD–D_2O at the reflux for 3 hr or comparable conditions used to exchange α-pyridine 1-oxide protons,[18a,c,19] gave us a mixture containing also some pyridine 1-oxide-d_3 as judged by the high intensity of the ion, *m/e* 98, in the mass spectrum. The following method is recommended. A solution of freshly distilled pyridine 1-oxide (15 g, 0.16 mole) in D_2O (25 ml, 1.25 mol) was heated in a Monel bomb at 200° for 30 hr. After cooling, solvents were removed at 30 mm and the residue was redissolved in D_2O (25 ml) and heated once more as above. The solution was evaporated at 30 mm and the residue distilled, bp 108° (0.7 mm), to give a colorless solid (14.9 g, 96%): pmr ($CDCl_3$), δ 7.35 (s), compared to natural pyridine 1-oxide, δ 8.30 (m, H_2, H_6), 7.35 (m, H_3, H_4, H_5); mass spectrum (70 eV), base peak *m/e* 97 with *m/e* 96 less than 5% of base peak and no peak at *m/e* 95 for starting material.

1-Acetyl-2-acetoxy-3,6-di-*t*-butylmercapto-1,2,3,6-tetrahydropyridine-2,6-d_2.—The use of pyridine 1-oxide-2,6-d_2 in expt A[2] and subsequent work-up as described for **1a** above yielded the product: mp 116–117°; ir, 1745, 1680, 1660 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 361 (4), 273 (4), 272 (24), 271 (3), 213 (4), 212 (25), 182 (5), 171 (6), 170 (46), 169 (15), 156 (13), 140 (16), 132 (11), 124 (6), 115 (9), 114 (49), 113 (57), 112 (9), 98 (18), 90 (4), 85 (4), 84 (3), 83 (4), 82 (44), 81 (13), 80 (4), 75 (4), 69 (6), 60 (6), 59 (4), 58 (5), 57 (100), 56 (8), 55 (7), 54 (3), 53 (5), 52 (3), 51 (3), 45 (9), 43 (45), 42 (4), 41 (48), 40 (10), 39 (14); at 13-eV, *m/e* 169 and 113 predominated. These ions picked up only H· and not D· since *m/e* 171 and 115 did not change with increase of electron voltage.

1-Acetyl-2-acetoxy-3,6-di(methylmercapto)-1,2,3,6-tetrahydropyridine (11).—After the distillation of the sulfides in expt C,[2] chromatography on alumina (200 g) gave on elution with benzene (300 ml) and ether (200 ml) a solid (0.8 g, 3%) which crystallized from petroleum ether; mp 115–117°; uv max (methanol), 200 mμ (log ε 4.11); ir, 1745, 1670, 1660 cm^{-1};

(16) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(17) See footnote 29 in ref 2.

(18) (a) Y. Kawazoe, M. Ohnishi, and Y. Yoshioka, *Chem. Pharm. Bull.* (Tokyo), **12**, 1384 (1964); (b) *ibid.*, **15**, 1225 (1967); (c) M. Tsuda and Y. Kawazoe, *ibid.*, **16**, 702 (1968).

(19) J. P. Schaefer and J. L. Bertram, *J. Amer. Chem. Soc.*, **89**, 4121 (1967).

mass spectrum (70 eV), *m/e* (rel intensity) 276 (1), 275 (4), 228 (38), 168 (23), 138 (12), 128 (6), 127 (12), 126 (100), 125 (27), 112 (8), 111 (6), 96 (42), 90 (17), 80 (52), 79 (25), 78 (12), 68 (8), 54 (7), 53 (17), 52 (10), 51 (6), 48 (8), 47 (14), 46 (5), 45 (20), 43 (84), 41 (10), 39 (10), 33 (7), 32 (6). At 8.5–10 eV, the following ions were prominent, *m/e* 275, 228 (base peak), 168, 125, and 79. At 13 eV, *m/e* 126 appeared and at 20 eV became more prominent than the one at *m/e* 125, and that at *m/e* 80 started to be noticeable. This once more points to a ion–molecular interaction of *m/e* 125 as discussed above.

Anal. Calcd for $C_{11}H_{17}NO_3S_2$: C, 48.00; H, 6.18; N, 5.09; S, 23.27. Found: C, 48.11; H, 6.40; N, 5.17; S, 23.22.

1-Acetyl-2-acetoxy-4-methyl-3,6-di-*t*-butylmercapto-1,2,3,6-tetrahydropyridine (**1b**).—Chromatography of the residue from expt D[2] yielded **1b** on elution with benzene (7 g, 6%); mp 105–107°; uv max (hexane), 195 mμ (log ε 4.39), (methanol) 204.5 mμ (log ε 4.39); ir, 1748, 1665 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 373 (1), 284 (10), 224 (6), 194 (7), 182 (12), 181 (9), 168 (3), 152 (17), 132 (11), 126 (18), 125 (56), 124 (5), 110 (22), 94 (17), 93 (35), 92 (10), 90 (11), 75 (9), 66 (9), 65 (7), 60 (8), 57 (100), 56 (14), 55 (8), 53 (9), 45 (13), 43 (48), 41 (58), 39 (25), 32 (12); at 13 eV, ions *m/e* 181, 125 (base peak), and 94 are most prominent. Increase in electron voltage promoted the concentration of *m/e* 182, in particular.

Anal. Calcd for $C_{18}H_{31}NO_3S_2$: C, 57.90; H, 8.31; N, 3.75; S, 17.15. Found: C, 57.92; H, 8.40; N, 3.82; S, 17.12.

1-Acetyl-2-acetoxy-4-phenyl-3,6-di-*t*-butylmercapto-1,2,3,6-tetrahydropyridine (**1c**) could not be found in expt F[2] but was procured in the following way. Acetic anhydride (100 ml) was added to a mixture of 4-phenylpyridine 1-oxide (15.5 g, 0.1 mol) and *t*-butyl mercaptan (32 ml, 0.3 mol) and the resultant solution was heated to 95° for 3 hr. The solution was cooled somewhat and a low-boiling fraction was distilled at 95° (steam bath) *in vacuo* (20–30 mm). This liquid was not examined further. One-half of the residue was dissolved in petroleum ether and the solid was collected after 48 hr. Recrystallization from aqueous ethanol gave **1c** (1.1 g, 5%): mp 140–142°; uv max (hexane), 200 mμ (log ε 4.63), 248 (log ε 4.24); (methanol) 204 mμ (log ε 4.63), 249 mμ (log ε 4.32); ir, 1752, 1675 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 376 (M − 59, 0.8), 347 (8), 346 (M − 89, 38), 286 (7), 244 (18), 243 (9), 214 (8), 189 (11), 188 (43), 187 (63), 186 (46), 172 (20), 157 (6), 156 (43), 155 (52), 154 (20), 132 (7), 128 (9), 127 (10), 115 (18), 102 (5), 90 (6), 77 (6), 75 (6), 60 (6), 57 (100), 56 (6), 55 (5), 51 (6), 50 (6), 45 (9), 43 (42), 41 (40), 39 (13), 32 (9), 29 (20); at 13 eV, ion *m/e* 346 was the base peak. Again, the ion, *m/e* 243, was most sensitive to eV changes as explained above for **3a**.

Anal. Calcd for $C_{23}H_{33}NO_3S_2$: C, 63.44; H, 7.59; N, 3.21; S, 14.71. Found: C, 63.49; H, 7.90; N, 3.17; S, 14.40.

1-Acetyl-4-*t*-butyl-2,3,6-tri-*t*-butylmercapto-1,2,3,6-tetrahydropyridine (**12**) **and 1-Acetyl-2-acetoxy-3,6-di-*t*-butylmercapto-4-*t*-butyl-1,2,3,6-tetrahydropyridine** (**1d**).—The residue from expt E[2] was chromatographed on alumina. Elution with benzene furnished mixtures (thin layer chromatography). Crystallization of the residues from the early eluates from petroleum ether gave **12** (5.85 g, 13%): mp 156–157; uv max (hexane), 194 mμ (log ε 4.34), (methanol) 205 mμ (log ε 4.35); ir, 1680 cm^{-1} (C=O of amide); mass spectrum (70 eV), *m/e* (rel intensity) 356 (11), 244 (1), 210 (4), 185 (1), 178 (4), 168 (6), 136 (10), 135 (16), 121 (7), 120 (42), 94 (5), 92 (16), 90 (9), 75 (5), 65 (6), 59 (5), 58 (5), 57 (100), 56 (12), 55 (11), 51 (9), 50 (5), 43 (18), 42 (6), 41 (67), 40 (5), 39 (26), 32 (15), 29 (31). *Anal.* Calcd for $C_{23}H_{43}NOS_3$: C, 62.02; H, 9.66; N, 3.14; S, 21.55. Found: C, 62.23; H, 9.76; N, 3.27; S, 21.47.

Concentration of the later eluates yielded a solid which on repeated recrystallization from petroleum ether gave **1d**: mp 98–100°; uv showed end absorption (methanol), 200 mμ (log ε 4.19); ir, 1795, 1670, cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 328 (7), 327 (20), 326 (M − 89, 93), 284 (3), 266 (10), 228 (5), 225 (4), 224 (17), 223 (7), 211 (7), 210 (54), 194 (10), 178 (10), 169 (13), 168 (95), 167 (25), 153 (6), 152 (25), 137 (6), 136 (50), 135 (16), 134 (6), 132 (8), 125 (27), 121 (17), 120 (52), 106 (10), 92 (14), 90 (7), 77 (5), 75 (5), 65 (4), 60 (5), 59 (5), 58 (5), 57 (100), 56 (7), 55 (8), 45 (9), 43 (58), 41 (45), 39 (15), 32 (10), 29 (22); at 14 eV *m/e* 326 was the base peak. The ion, *m/e* 223, was again most sensitive to changes in electron voltage.

Anal. Calcd for $C_{21}H_{37}NO_2S_2$: C, 60.70; H, 8.98; N, 3.37; S, 15.40. Found: C, 60.80; H, 8.91; N, 3.54; S, 15.33.

1-Acetyl-2,6-diacetoxy-3,5-dimethyl-3-*t*-butylmercapto-1,2,3,6-tetrahydropyridine (**13**).—The residue from expt J[2] was chromatographed on alumina. Elution by benzene–ether (400:300 ml) gave **13** which crystallized from petroleum ether; mp 125–127° (1.2 g, 3%); uv max (hexane), 198 mμ (log ε 4.38), (methanol) 204 mμ (log ε 4.33); ir, 1750, 1680, 1670 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 357 (1), 298 (1), 269 (7), 268 (45), 226 (37), 182 (2), 166 (5), 140 (5), 124 (100), 108 (17), 107 (8), 106 (9), 96 (7), 57 (11), 43 (32), 41 (10); at 10–13 eV, the following ions stood out, *m/e* 357 (base peak), 268, 226, 166, 124, and 107. Ion *m/e* 108 is the 3,5-lutidinium ion and appeared as electron voltage increased, presumably by an ion–molecule interaction.

Anal. Calcd for $C_{17}H_{27}NO_5S$: C, 57.14; H, 7.56; N, 3.92; S, 8.96. Found: C, 57.41; H, 7.76; N, 3.91; S, 9.11.

Registry No.—Acetic anhydride, 108-24-7; **1a**, 18794-20-2; **1a** (2,6-d_2), 18794-21-3; **1b**, 18794-22-4; **1c**, 18794-23-5; **1d**, 18794-24-6; **11**, 18833-88-0; **12**, 18794-25-7; **13**, 18833-89-1; pyridine 1-oxide-2,6-d_2, 3739-95-5.

Acknowledgments.—We are indebted to Dr. Charles L. Bell for many valuable discussions of the various spectra and to Mr. Kenneth F. King for technical help. We thank the Research Board of the University of Illinois for funds to purchase a high-pressure bomb.