in 20 mL of acetone containing 0.2 mL of water and 1 g of $NaHCO_3$. The resulting solution was stirred for 25 min at 0 °C. Removal of solvent under vacuum gave a white solid, which was dissolved in 25 mL of hot ligroin and 25 mL of hot benzene. The solution was filtered, and the solvents were removed under vacuum to give 1.2 g (80%) of a white solid: IR ($CHCl_3$) 3400 (w), 1755 (s), 1720 (m), 1490 (m), 1455 (w), 1365 (m) cm^{-1}. Volhard titration for chlorine[12] gave 88.6 ± 2.1% of the theoretical value for **2a**. Recrystallization from pentane gave a white solid, mp 88–89 °C. Volhard titration was still low in chlorine (82.8 ± 1.3% of expected value) due to facile conversion of **2a** to the diazetidinedione.

Hydrolysis of **4a** under less carefully controlled conditions, or even leaving **4a** loosely stoppered for a few days at room temperature, gave diazetidinedione **1a** as the major product, isolated from the mixture by sublimation (75 °C, 0.1 torr): mp 88–90 °C (lit.[6] mp 89–90 °C); IR ($CHCl_3$) 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s).

Isopropyl[(isopropylamino)carbonyl]carbamic Chloride (2b). Phosgene was passed through a solution of diisopropylcarbodiimide in methylene chloride at 0 °C until the infrared spectrum showed no remaining carbodiimide stretch (2100 cm^{-1}), ca. 15 min. Removal of the volatile components under vacuum gave 88% of a pale green oil (**4b**):[7b] IR ($CHCl_3$) 1745 (s), 1665 (m) cm^{-1}. To 29.5 g (0.13 mol) of **4b** in 200 mL of acetone at 0 °C was added 20 mL of water, and the solution was stirred for 35 min. The solvents were removed under reduced pressure, and the residue was recrystallized from ligroin to give 16.4 g (61%) of white crystals: mp 61–64 °C (lit.[5a] mp 63 °C); IR ($CHCl_3$) 3430 (w), 3360 (w), 1725 (s), 1505 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.28 (d, 6 H, J = 7 Hz), 1.43 (d, 6 H, J = 7 Hz), 4.2 (m, 2 H), 6.5 (br, 1 H).

Cyclohexyl[(cyclohexylamino)carbonyl]carbamic Chloride (2c). Addition of phosgene to dicyclohexylcarbodiimide as for **4b** gave a quantitative yield of **4c**:[7a] IR ($CHCl_3$) 1735 (s), 1662 (m) cm^{-1}. A solution of **4c** (5.3 g, 17.4 mmol) in 30 mL of acetone and 25 mL of water was allowed to stand for 20 h. The resulting white needles were isolated by filtration: yield 1.70 g (34%); mp 122–123 °C [lit.[5a] mp 127–128 °C (hexane)]. An additional 1.66 g (33%), mp 120–121 °C, was obtained by extraction, solvent removal, and recrystallization from hexane. The total yield of recrystallized **2c** was 3.36 g (67%). Further recyrstallizations, either from hexane or acetone–water, did not raise the melting point above 122–123 °C: IR ($CHCl_3$) 3420 (w), 1715 (s), 1495 (m) cm^{-1}; NMR ($CHCl_3$) δ 1.0–2.1 (m, 20 H), 3.5–4.1 (m, 2 H), 6.0 (br, 1 H).

Anal. Calcd for $C_{14}H_{23}N_2O_2Cl$: C, 58.63; H, 8.08. Found: C, 58.90; H, 8.31.

1,3-Diisopropyldiazetidinedione (1b). Compound **2b** (2.63 g, 12.7 mmol) and 1.57 g (14.0 mmol) of Dabco in 50 mL ether were stirred for 1 h and filtered. Hydrogen chloride was bubbled through the filtrate, and the resulting suspension was again filtered. Removal of the ether gave 1.85 g (86%) of a clear oil, crystallized from pentane at −78 °C to give 1.19 g (55%) of white needles that melted to a clear oil below room temperature. The compound may also be distilled: bp 80–83 °C (14 torr); IR ($CHCl_3$) 1760 (s), 1450 (w), 1380 (m), 1315 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.33 (d, 12 H, J = 6 Hz), 3.7 (sept, 2 H, J = 6 Hz); mass spectrum m/e (relative intensity) 170 (M^+, 0.5), 155 (2), 86 (2), 85 (12), 84 (2), 71 (4), 70 (100).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29. Found: C, 56.28; H, 8.06.

1,3-Dicyclohexyldiazetidinedione (1c) was prepared as described for **2b**. Removal of the ether under vacuum and recrystallization of the residue from hexane at −15 °C gave an 84% yield of white crystals: mp 92–94 °C; IR ($CHCl_3$) 1750 (s), 1440 (w), 1390 (w), 1360 (w), 1340 (w) cm^{-1}; NMR ($CDCl_3$) δ 1.1–2.1 (m, 20 H), 3.1–3.4 (m, 2 H); mass spectrum, m/e (relative intensity) 250 (M^+, 6), 222 ($M^+ - CO$, 1), 207 (1), 169 (2), 168 ($M^+ - C_6H_{10}$, 5), 126 (41), 125 (M^+ - c-$C_6H_{11}NCO$, 100).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86. Found: C, 67.16; H, 8.94.

1,3-Dimethyldiazetidinedione (1d). Methyl[(methylamino)-carbonyl]carbamic chloride (**2d**) was prepared according to the procedure of Ulrich et al.:[5a] mp 31–32 °C (lit.[5a] mp 36 °C); IR ($CHCl_3$) 1730 (s), 1530 (m) cm^{-1}. Treatment of **2d** with Dabco as described for **2b**, removal of the solvent under vacuum, and recrystallization from hexane gave a 79% yield of white volatile plates: mp 96–98 °C (lit.[2d] mp 94–95 °C); IR ($CHCl_3$) 1780 (s), 1725 (w), 1440 (w), 1370 (w) cm^{-1}; NMR ($CDCl_3$) δ 2.86 (s); mass spectrum, m/e (relative intensity) 114 (M^+, 2), 86 (9), 70 (12), 59 (3), 58 (67), 57 (100).

Reaction of Isopropyl[(isopropylamino)carbonyl]carbamic Chloride (2b) with Potassium *tert*-Butoxide. Compound **2b** (2.06 g, 10 mmol) and potassium *tert*-butoxide (1.25 g, 11 mmol) were refluxed together in 12 mL of dry tetrahydrofuran under nitrogen for 10 h. The mixture was cooled to 0 °C, diluted with water, and extracted with pentane. The pentane was dried ($MgSO_4$) and removed under vacuum to give 2.74 g of an oil and solid. NMR analysis of the mixture was consistent with the presence of two products, *tert*-butyl isopropylcarbamate **6** (63%) and triisopropyltriazinetrione **7** (29%). The products were separated by GLC (15% SE 30 on Chromosorb W, 6 ft × 0.25 in., temperature programmed at 140–200 °C at 5 °C/min). The structure of **6** was confirmed by spectral comparison and a mixed melting point with an authentic sample. The triazinetrione **7** was a white solid: mp 103–104 °C; IR ($CHCl_3$) 1690 (s), 1470 (m), 1435 (s), 1425 (s), 1370 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.46 (d, 18 H), 5.0 (sept, 3 H); mass spectrum, m/e (relative intensity) 256 (6), 255 (M^+, 39), 240 (21), 214 (44), 198 (19), 172 (42), 171 (13), 170 (6), 57, (100).

***tert*-Butyl *N*-Isopropylcarbamate (6).** To 176 mg (2.1 mmol) of isopropyl isocyanate in 25 mL of ligroin at 0 °C was added a few milligrams of $SnCl_2 \cdot H_2O$[13] and 154 mg (2.1 mmol) of *tert*-butyl alcohol. The reaction was warmed to room temperature and then refluxed for 2.5 h. The warm reaction mixture was filtered and the filtrate taken to dryness under aspirator vacuum. The residue was sublimed at 14 torr to give 147 mg (45%) of white crystals:[14] mp 70.5–72.5 °C; IR ($CHCl_3$) 3440 (w), 1705 (s), 1495 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 6 H, J = 6 Hz), 1.47 (s, 9 H), 3.8 (m, 1 H), 4.3 (br, 1 H).

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Registry No.—**4a,** 55871-88-0; **4b,** 13829-15-7; **4c,** 13236-48-1; **6,** 51170-55-9; **7,** 67463-81-4; phosgene, 75-44-5; isopropyl isocyanate, 1795-48-8; *tert*-butyl alcohol, 75-65-0.

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1,1-Bis(acylthio)alkanes Formed by Base-Catalyzed Condensation of Thiol Acids

Larry Sternson

Department of Pharmaceutical Chemistry, The University of Kansas, Lawrence, Kansas 66044

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As part of our continuing interest in using organosulfur-containing nucleophilic compounds as analytical reagents, the behavior of thiol acids was studied in basic solutions. Ether solutions containing equimolar quantities of thiolacetic acid and tertiary amine (pyridine or triethylamine) were unstable, as evidenced by the appearance of elemental sulfur (mp 116–117 °C) when the mixture was allowed to stand at room

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Table I. 1,1-Bis(acylthio)alkane Synthesis[a]

$RCH(SCR)_2$ (R = O)

R	registry no.	bp, °C (torr)	mp, °C	% yield[b]
CH_3	20266-80-2	41 (0.002)		97
C_2H_5	67584-26-3	60 (0.002)		90
C_3H_7	67584-27-4	82 (0.003)		87
C_6H_5	13286-78-7		137–138	93

[a] Satisfactory analytical data (±0.4% for C, H, S) were reported for all new compounds listed in the table. [b] Calculated on the basis that 3 mol of thiol acid are consumed in the formation of 1 mol of alkane.

temperature for 8 h. This solid was identified by comparison of physical properties with an authentic sample of sulfur.

Thin-layer chromatographic monitoring of the reaction mixture on silica gel plates indicated that the thiolacetic acid had been consumed with concomitant appearance of a new band in the chromatogram. This product was subsequently isolated by distillation [bp 41 °C (0.002 torr)] and was tentatively identified as 1,1-bis(acetylthio)ethane (1) from NMR [($CDCl_3$) δ 2.4 (s, 6, $CH_3C(S)=O$), 3.8 (q, 1, HCS_2), 1.4 (d, 3, CH_3CS_2)], IR [(CCl_4) 1690 cm^{-1} (C=O)], mass spectral (M^+ 178), and elemental analysis data (eq 1). The structure was

$$CH_3COSH \xrightarrow{R_3N} \underset{\mathbf{1}}{CH_3CH(SCCH_3)_2} + S + H_2O \qquad (1)$$

verified by alternative preparation of 1 from 1,1-dimethoxyethane plus thiolacetic acid.[1] Thiol acid (3 mol) reacts in the presence of base to form the corresponding dithiolacylate. In the process, 1 mol of thiol acid is reduced to the aldehyde oxidation state with expulsion of elemental sulfur. Acetaldehyde could not be detected in the reaction mixture, suggesting that the reaction may not proceed by initial formation of an aldehyde intermediate. 1,1-Bis(acylthio)alkanes have been synthesized previously by reaction of *gem*-dithiols with acid anhydrides[2] and by reaction of *gem*-thiocyanates with thiol acids.[3]

The synthetic utility of this reaction was explored using several thiol acids. The yields and physical properties of the resulting 1,1-bis(acylthio)alkanes are shown in Table I. The reaction proceeded efficiently with all the thiol acids that were tested; so this reaction appears to be a useful synthetic route to symmetrical 1,1-bis(acylthio)alkanes and may, for some applications, be a useful pathway for reduction from the acid to aldehyde oxidation state.

Experimental Section

Thiol acids (0.15 mol) were dissolved in ether (75 mL) containing 0.15 mol of triethylamine or pyridine. The solutions were allowed to stand at room temperature for 8 h, after which time they were cooled to 0 °C in an ice bath. The orange precipitate that had formed was removed by filtration and the solution was then acidified with 10 mL of cold 10% hydrochloric acid solution followed by the addition of 10 mL of cold water. An oil separated and was taken up in 25 mL of ether. The aqueous layer was then extracted with three 25-mL portions of ether; the organic phases were combined and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue was distilled under reduced pressure.

Registry No.—Thiolacetic acid, 507-09-5; thiolpropionic acid, 1892-31-5; thiolbutyric acid, 3931-64-4; thiolbenzoic acid, 98-91-9.

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Another Pathway of the Reaction of Thionyl Chloride with Active Methylene Compounds. Reaction of Anthrone with Thionyl Chloride

Kitaro Oka* and Shoji Hara

Tokyo College of Pharmacy, Horinouchi 1432-1, Hachioji, Tokyo 192-03, Japan

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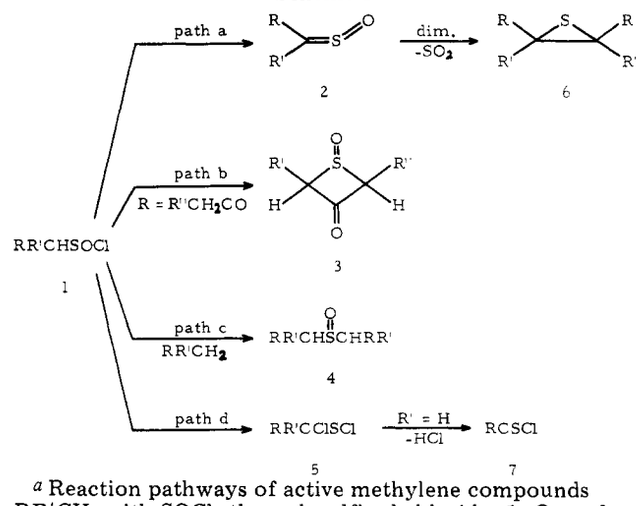
In the reaction of thionyl chloride and active methylene compounds, several pathways may be considered according to the amount of thionyl chloride employed and the structure of the substrate. Sulfinyl chlorides 1 (Scheme I), which had been believed to be primary products,[1] were isolated by Pizey and Symeonides.[2a] The chemical behavior of such sulfinyl chlorides in reaction medium includes the following: (a) intramolecular dehydrochlorination to give a sulfine (**2**, path a)[3] or a thietanone *S*-oxide (**3**, path b);[2a,b] (b) intermolecular dehydrochlorination to give a sulfoxide (**4**, path c);[3] or (c) Pummerer-type rearrangement, leading to an α-chlorosulfenyl chloride (**5**, path d).[4]

Paths a and b proceed with equimolar or slightly excessive amounts of thionyl chloride, while path c requires a half-molar amount of reagent and path d a large excess of reagent.[5] Formation of other products might be explained in terms of further chemical modifications; for instance, (a) olefins from malonates by Ireland and Pizey[6] are understandable in terms of dimerization and desulfurization of the sulfine via thiirane **6**[6,7] and (b) thioacyl chlorides **7** from acetophenone and other active methyl compounds are explained by dehydrochlorination of the sulfenyl chloride **5**.[8] However, one can find other examples in the literature which cannot be explained by these proposals. Takimoto and Krbechek[9] have reported that anthrone in hot thionyl chloride gave an unstable material of unknown structure which was converted to olefin **16** (Scheme II) by treatment with malononitrile. At first, we considered that this intermediate might be α-chlorosulfenyl chloride **17**, owing to our consideration that such sulfenyl chlorides might be easily converted to olefins when treated with a strong carbon acid via thiocarbonyl ylide and its electrocyclized thiirane.[10] However, our efforts to isolate it failed in spite of its expected stability.

When anthrone 8 was treated with 3 molar equiv of thionyl chloride at room temperature, a crystalline product was obtained quantitatively after vigorous evolution of hydrogen

Scheme I[a]



[a] Reaction pathways of active methylene compounds $RR'CH_2$ with $SOCl_2$ through sulfinyl chlorides 1. One of the substituents or both of them are π-accepting groups such as C=O, C=N, etc.

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