ammonia evolution ceased (~5 days). A small amount of solid, which formed during that time, was filtered and the filtrate was reduced to a dark-brown, gummy semisolid by removing solvent under vacuum. This material was stirred with 600 ml of water for 4 hr and filtered to give 33.4 g (43%) of a yellow powder, mp 95–100° (lit.[10] mp 98–101°).

A mixture of *N*,*N*′-bis(2-hydroxypropyl)dithiooxamide (113.5 g, 0.48 mol) in toluene (575 ml) was treated with four 60-g portions of thionyl chloride over a period of 1.5 hr. The reaction mixture was then heated at 45–50° for 1.5 hr, after which the resulting gold-colored dication was filtered and found to weigh 66.9 g (51%), mp 118–131°.

Neutralization of the dication (66.9 g) with a solution of sodium bicarbonate (42.5 g, 0.5 mol) in 450 ml of water gave 49 g (100%) of a dark-brown solid. Recrystallization from *n*-hexane yielded a cream-colored powder, mp 92–93.5°. *Anal.* Calcd: C, 48.0; H, 6.00; N, 14.0; S, 32.0. Found: C, 48.2; H, 6.22; N, 13.9; S, 31.9.

The nmr spectrum ($CDCl_3$) consisted of a complex multiplet at 4.75–3.80 ppm ($-CH_2CH-$) and a doublet centered at 1.38 ppm (CH_3-).

Registry No.—**1**, 41601-87-0; **1′** 2Cl⁻, 41601-88-1; **2**, 41601-89-2; **2′** 2Cl⁻, 41601-90-5; **3**, 41601-91-6; **3′** 2Cl⁻, 41601-92-7; **4**, 41601-93-8; **4′** 2Cl⁻, 41601-88-1; *N*,*N*′-bis(2-hydroxyethyl)dithiooxamide, 120-86-5; *N*,*N*′-bis(2-hydroxypropyl)dithiooxamide, 3815-26-7; *l*-2-amino-1-propanol, 35320-23-1; *N*,*N*′-bis(2-hydroxy-1-methylethyl)dithiooxamide, 41601-97-2; 1-amino-2-propanol, 78-96-6; dithiooxamide, 79-40-3.

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[10] R. N. Hurd, G. DeLaMater, G. C. McElheny, R. J. Turner, and V. H. Wallingford, *J. Org. Chem.*, **26**, 3980 (1961).

Thioimidates and Ketene Mercaptals from Ketenimines

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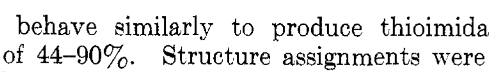
The addition of mercaptans to such heterocumulenes as ketenes, isocyanates, and carbodiimides has been found to occur smoothly and in good yield to produce thio esters,[2] thiocarbamates,[3] and S-substituted isothioureas,[4] respectively. As a continuation of a study of the chemistry of ketenimines[5] and mercaptan addition to heterocumulenes, we have investigated the reactions of mercaptans and ketenimines.

When diphenylketene-*N*-(*p*-bromophenyl)imine (**1a**) is treated with excess thiophenol at the temperature of refluxing benzene, the corresponding thioimidate (**2**) is formed in 72% yield (eq 1). Other *N*-aryl ketenimines behave similarly to produce thioimidates in yields of 44–90%. Structure assignments were based on ir data (loss of the ketenimine absorption at 2000 cm^{-1} and appearance of the imine absorption at approximately 1640 cm^{-1}), nmr data (absorption for the benzhydryl proton at δ 5 ppm), and elemental analyses. All thioimidates produced from thiophenol were crystalline solids and were easily purified. Aliphatic mercaptans as represented by the ethyl and *n*-propyl substituents also add to ketenimines to yield crystalline thioimidates in good yields (Table I).

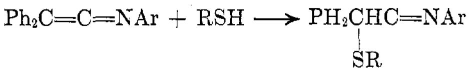


$$\underset{\textbf{1a}}{Ph_2C{=}C{=}NAr} + RSH \xrightarrow{80^\circ} \underset{\textbf{2a}}{Ph_2CH\underset{|}{\overset{}{C}}{=}NAr}\quad (1)$$

$$\qquad\qquad\qquad\qquad\qquad\quad SR$$

Table I

Thioimidates from Ketenimines[a]



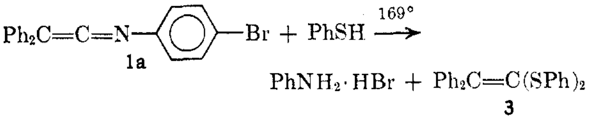
$$Ph_2C{=}C{=}NAr + RSH \longrightarrow PH_2CH\underset{\substack{|\\ SR}}{C}{=}NAr$$

Sample	Ar	R	Yield of **2**, %	Mp, °C
a	*p*-Bromophenyl	Phenyl	72	92–93
b	*m*-Bromophenyl	Phenyl	60	82.5–83
c	*p*-Chlorophenyl	Phenyl	73	83.5–84.0
d	*m*-Chlorophenyl	Phenyl	44	75.0–75.5
e	Phenyl	Phenyl	45	80.0–81.0
f	*p*-Tolyl	Phenyl	64	85–85.5
g	*p*-Anisyl	Phenyl	81	106.5–107.5
h	*p*-Fluorophenyl	Phenyl	61	91.5–92.5
i	*p*-Bromophenyl	Ethyl	71	95–95.5
j	*p*-Bromophenyl	*n*-Propyl	90	88.5–89.0

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all thioimidates listed in this table: Ed.

Although these reactions were first performed with irradiation and presumed to occur by radical addition, it was subsequently found that light is not needed. Furthermore, the same products are obtained in comparable yields if the sodium salt of the mercaptans is employed.

When **1a** was treated with excess thiophenol at 169° (refluxing thiophenol), rather than 80°, no thioimidate was found. Instead, aniline hydrobromide precipitate from solution and work-up of the reaction mixture yielded only diphenylketene diphenylmercaptal[6] (**3**) (eq 2). This reaction is apparently an acid-catalyzed

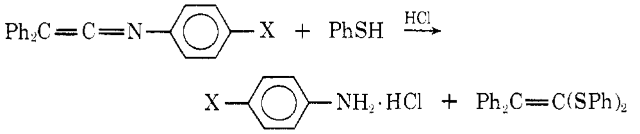


1a **3** (2)

process and the HBr catalyst is produced through a hydrogenolysis reaction of the aryl bromide of **1a**. To test this hypothesis, **1e** was treated with excess thiophenol at 169° with the addition of HCl; **3** was obtained from the reaction in 68% yield. Table II con-

Table II

Ketene Mercaptals from Ketenimines



X	Yield, %
H	67.7
p-Cl	52
m-Cl	64
p-CH_3	42.5
p-OCH_3	42.5

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[1] NDEA Predoctoral Fellow, 1969–1972.

[2] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. B*, 1303 (1970).

[3] S. Ozaki, *Chem. Rev.*, **72**, 457 (1972).

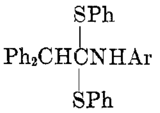
[4] P. Schlack and G. Keil, *Justus Liebigs Ann. Chem.*, **661**, 164 (1963); M. Busch, G. Blume, and E. Pungs, *J. Prakt. Chem.*, **79**, 513 (1909).

[5] For previous reports see M. W. Barker and R. H. Jones, *J. Heterocycl. Chem.*, **9**, 555 (1972); M. W. Barker and J. D. Rosamond, *ibid.*, **9**, 1147 (1972); M. W. Barker, L. L. Combs, and J. T. Gill, *ibid.*, **9**, 77 (1972); and references cited therein.

[6] A. Schonberg and L. V. Vargha, *Justus Liebigs Ann. Chem.*, **483**, 176 (1930).

tains the data for the general reaction of *N*-aryl ketenimines and thiophenol under acid catalysis. Also, it was observed that the thioimidates yield ketene mercaptals when treated with excess thiophenol and HCl.

Several conclusions can be drawn from these observations concerning the mechanism of ketene mercaptal production. The ketenimine presumably undergoes monoaddition to yield the thioimidate, which is converted to the mercaptal with acid catalysis. The intermediate is probably the diadduct **4**. This intermediate would be expected to eliminate aniline at the reaction temperature to yield the mercaptal, a process similar to the preparation of ketene mercaptals by Volger and Arens[7] in which compound **5** undergoes thermal elimination of RSH to produce the ketene mercaptal.



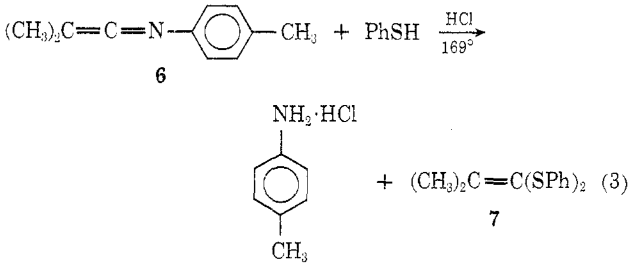
$Ph_2CHC(SPh)_2NHAr$

4

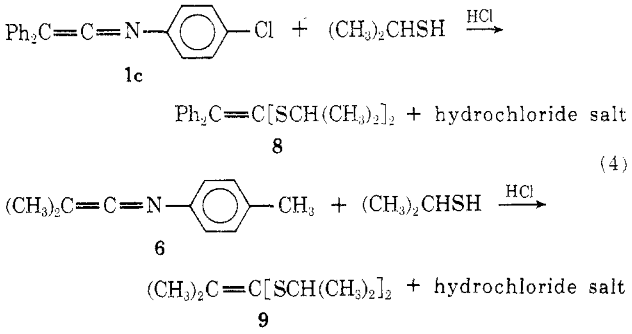
$R_2CHC(SR)_3$

5

In an effort to determine the generality of the synthesis of ketene mercaptals from ketenimines, attempts were made to produce ketene mercaptals containing aliphatic as well as aromatic substituents. When dimethylketene-*N*-(*p*-tolyl)imine (**6**) is treated with excess thiophenol at reflux with added HCl and then the reaction mixture is distilled, a fraction boiling at 168° (0.8 mm) is obtained (86% yield) which has an elemental analysis compatible with **7** and has nmr absorptions for the methyl protons at δ 1.88 and the phenyl protons at δ 6.2.



Treatment of ketenimine **1c** or **6** with 2-propanethiol and HCl yielded oily liquids (eq 4). The expected product from ketenimine **1c** is **8** and that from **6** is **9**.



The product thought to be **9** was obtained in a crude yield of 24% and possessed nmr absorption at δ 1.22 [d, $-CH(CH_3)_2$], about 2.5 [m, $-CH(CH_3)_2$], and 2.07 [s, $(CH_3)_2C=$]. Likewise, **8** has an nmr spectrum compatible with the proposed structure. However, distillation did not yield analytically pure samples of these two particular ketene mercaptals.[8] Since other preparations are available for these last two ketene mercaptals,[7,9] the additional isolation work was not performed.

In conclusion, the preparation of thioimidates from ketenimines and mercaptans has been shown to be an effective reaction limited only by the availability of ketenimines.[10] The preparation of the synthetically important ketene mercaptals[11] from the reaction of ketenimines and mercaptans under acid catalysis gave insolable products only when thiophenol was employed as the mercaptan. However, the ease of producing these ketene mercaptals by this process makes it potentially useful.

Experimental Section[12]

Preparation of Thioimidates.—The synthesis of phenyl *N*-*p*-chlorophenyldiphenylthioacetimidate (**2c**) is typical for preparation of the thioimidates in Table I prepared from ketenimines and thiophenol. A solution of 5 g (0.017 mol) of diphenylketene-*N*-(*p*-chlorophenyl)imine and 10 g of thiophenol in 50 ml of benzene was heated to reflux for 24 hr. The benzene and excess thiophenol were removed at reduced pressure (aspirator) and the residue was dissolved in 50 ml of hot hexane. Slow cooling of the hexane solution resulted in the precipitation of 5 g (73%) of colorless crystals, mp 81–83°. The product exhibited an ir absorption of 1635 cm^{-1} indicative of the imine stretch and nmr absorptions at δ 5.0 (benzhydryl proton) and centered on 7.1 (aromatic protons). An analytical sample of the crude product from a similar run was prepared by recrystallization from hexane, mp 83.5–84.0°.

The thioimidates from ethyl and *n*-propyl mercaptan were prepared in a similar manner except for the temperature, which was kept compatible with the mercaptan (35° for ethyl and 60° for *n*-propyl).

Thioimidates **2a** and **2j** were also prepared by adding the sodium salt of thiophenol and of *n*-propyl mercaptan, respectively, to **1a**. The products were identical with those produced from the mercaptans and the yield by this procedure for **2a** was 55% and for **2j** was 49%.

Diphenylketene Diphenylmercaptal. A. From 1a and Thiophenol.—A solution of 5 g (0.014 mol) of **1a** and 4.7 g of thiophenol was heated to 169° for 24 hr. The excess thiophenol was removed under reduced pressure (aspirator) and the residue was extracted with hot hexane (2 × 15 ml). Concentration and cooling of the hexane solution afforded 4.8 g (84%) of pale yellow needles, mp 92.5–96.5°. Subsequent recrystallization from

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[7] H. C. Volger and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **76**, 847 (1957).

[8] The combination of aliphatic mercaptan smell and an inadequate ventilation system prevented in-depth studies on the isolation of these products.

[9] F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 1926 (1972).

[10] H. Bestman, J. Lienert, and L. Mott, *Justus Liebigs Ann. Chem.*, **718**, 24 (1968); C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).

[11] D. Borrmann, "Sauerstoffverbindungen II," Teil 4, in "Methoden der Organischen Chemie," Band VII, Teil 4, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1968, p 404.

[12] Melting points were determined on Fisher-Johns or Mel-Temp apparatus and are corrected. Infrared spectra were determined on a Perkin-Elmer Infracord in KBr, Nujol, and carbon tetrachloride. Nuclear magnetic resonance spectra were determined on either a Jeolco Minimar or a Varian A-60 spectrometer in carbon tetrachloride. Mass spectra were determined on either a Perkin-Elmer Model 270 or Hewlett-Packard Model 5930 mass spectrometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

hexane gave a sample melting at 111.0–111.5° (lit.[6] mp 112°). Product identification is based on the nmr (absorptions for aromatic protons at δ 7.2 and 7.35), hydrolysis with concentrated sulfuric acid in glacial acetic acid to diphenylacetic acid, and an elemental analysis which is compatible with the known compound. From the hexane-insoluble residue was obtained 2.05 g (82%) of aniline hydrobromide, mp 283–285°. Identification was made by converting the hydrobromide to aniline and comparing it with an authentic sample.

The other ketenimines listed in Table I did not yield a ketene mercaptal under these conditions.

B. From Ketenimines, Thiophenol, and Acid Catalysts.—A solution of 5 g (0.019 mol) of **1e** in 20 ml of thiophenol was heated to reflux for 3 hr. During this period of reflux dry HCl was introduced into the solution continuously. The excess thiophenol was removed under reduced pressure (aspirator), and the residue was extracted with hot hexane (4 × 25 ml). As the hexane solution cooled, 4.8 g (62.7%) of diphenylketene diphenylmercaptal, mp 108–110°, precipitated.

The other ketenimines in Table II were treated in a similar manner to give diphenylketene diphenylmercaptal. Subsequently it was observed that similar yields of **3** could be obtained from these ketenimines, thiophenol, and gaseous HCl in benzene solutions heated to reflux. Thus 80° is sufficient for the synthesis.

C. From Thioimidates.—A solution of 4 g (0.01 mol) of **2c** in 20 ml of thiophenol was heated to reflux for 45 min. Dry HCl was introduced continuously into the solution during reflux. Work-up of the reaction mixture as already described gave 2.1 g (53%) of **3**.

Dimethylketene Diphenylmercaptal.—A solution of 5 g (0.034 mol) of dimethylketene-*N*-(*p*-tolyl)imine in 30 ml of thiophenol was heated to reflux for 45 min. Dry HCl was introduced into the solution during reflux. The excess thiophenol was removed under reduced pressure (aspirator) and the residue was extracted with hot hexane. Removal of the hexane left 9.4 g (86%) of a yellow, oily liquid which was distilled twice to produce an analytical sample: bp 169° (0.8 mm); nmr (CCl_4) δ 1.88 [s, $(CH_3)_2C{=}$] and 6.2 (m, aromatic protons).

Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.59; H, 5.88. Found: C, 70.47; H, 5.86.

Attempted Synthesis of Dimethylketene Diisopropylmercaptal.—To a solution of 6.3 g (0.04 mol) of dimethylketene-*N*-(*p*-tolyl)imine in 20 ml of 2-propanethiol was added dry HCl. The reaction mixture immediately warmed to reflux and maintained reflux for 15 min. The excess 2-propanethiol was removed under reduced pressure (aspirator) and the residue was extracted with hot hexane. Removal of the hexane left 1.9 g (24%) of yellow liquid: nmr (CCl_4) δ 1.22 (d, 12), 3.07 (s, 6), and 2.5 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 204 (8.6), 161 (6.7), 129 (4.8), 120 (6.7), 119 (9.5), 114 (3.8), 87 (34.3), 86 (53.3), 85 (38.1), 75 (18.1), 72 (20.1), 59 (23.8), 53 (19.1), 43 (94.3), and 41 (100).

Attempted Synthesis of Diphenylketene Diisopropylmercaptal.—A solution of 5 g (0.016 mol) of **1c** in 40 ml of 2-propanethiol and 20 ml of benzene was heated to reflux for 4 hr while dry HCl was continuously added. Work-up in the usual manner left 5.3 g (98%) of yellow liquid: nmr (CCl_4) δ 1.07 (d, 12). 1.83 (s, 6) and 3.0 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 326 (4), 283 (97.7), 190 (19.3), 165 (100), 210 (24.5), 115 (6.8), 89 (13.6), 75 (8.0), 65 (3.2), 43 (9.1), and 41 (12.5).

Acknowledgment.—We wish to thank the Vice-President for Research and the Biological and Physical Science Institute of Mississippi State University for partial support of this effort.

Registry No.—**1a**, 29376-76-9; **1b**, 41563-33-1; **1c**, 17205-60-6; **1d**, 17518-16-0; **1e**, 14181-84-1; **1f**, 5110-45-2; **1g**, 40012-82-6; **1h**, 41563-37-5; **2a**, 41563-38-6; **2b**, 41563-39-7; **2c**, 41563-40-0; **2d**, 41563-41-1; **2e**, 41563-42-2; **2f**, 41563-43-3; **2g**, 41563-44-4; **2h**, 41563-45-5; **2i**, 41563-46-6; **2j**, 41563-47-7; **3**, 41563-48-8; **6**, 18779-86-7; **7**, 41563-50-2; **8**, 41563-51-3; **9**, 41563-52-4; thiophenol sodium salt, 930-69-8; *n*-propyl mercaptan sodium salt, 6898-84-6; thiophenol, 108-98-5; ethyl mercaptan, 75-08-1; *n*-propyl mercaptan, 107-03-9; aniline hydrobromide, 542-11-0; 2-propanethiol, 75-33-2.

The Synthesis of 1,3-Dithiolanone Derivatives

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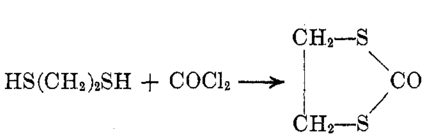
Although 1,3-dithiolan-2-one (**1**) has been prepared by the action of HgO on ethylene trithiocarbonate[1] or COS on ethylene sulfide,[2] the materials used are rather inaccessible. 1,3-Dithiolan-4-one derivatives (**2**) have not appeared in the literature. In this paper, we will describe a simple method of preparation of **1** and the synthesis of new compound **2**.

The compound **1** was readily prepared by the reaction of ethanedithiol with phosgene in the presence of



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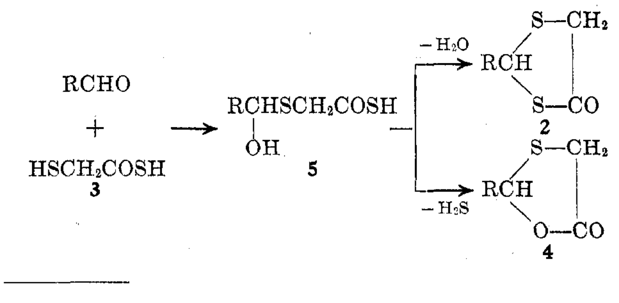
pyridine in fairly good yield. This reaction was carried out at 0°, but a large amount of polymeric substance was formed above 30°.

The 4-one derivatives **2** should be obtainable by condensation of mercaptothioacetic acid (**3**) with alde-

$$ClCH_2COCl \xrightarrow{H_2S} ClCH_2COSH \xrightarrow{KSH} \underset{\mathbf{3}}{HSCH_2COSH}$$

hydes. The acid **3**, which has not been reported in the literature, was obtained in a good yield from the reaction of chloroacetyl chloride with hydrogen sulfide, followed by treatment with potassium hydrogen sulfide.

The reactions of **3** with aldehydes were carried out in the presence of *p*-toluenesulfonic acid, and the expected product **2** was obtained in a yield of 25–45%, together with the corresponding 1,3-oxathiolan-5-one (**4**). Considering the formation of these two products, compound **5** was assumed to be the reaction interme-



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(1) C. G. Overberger and P. V. Bonsigner, *J. Amer. Chem. Soc.*, **80**, 5427 (1958).

(2) V. S. Etlis, L. N. Grobov, and G. A. Razuvaev, *Zh. Obshch. Khim.*, **32**, 2940 (1962); *Chem. Abstr.*, **58**, 7817a (1963).