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 \times 25 ml). As the hexane solution cooled, 4.8 g (62.7%) of diphenylketene diphenyl-mercaptal, 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.

С. 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 (CCl₄) δ 1.88 [s, $(CH_3)_2C=$] and 6.2 (m, aromatic protons).

Anal. Calcd for C16H16S2: 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 (CCl₄) 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 (CCl₄) § 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).

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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; 10, 17510-10-0, 1e, 17131-07-1, 11, 0110-10 2, 1g, 10512 02 0, 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; - 41563-52-4; think and an analysis of the set of th 9, 41563-52-4; thiophenol sodium salt, 930-69-8; n-propyl mercaptan sodium salt, 6898-84-6; thiophenol, 108-98-5; ethvl 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 trithiocarbonate¹ 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

$$HS(CH_2)_2SH + COCl_2 \longrightarrow \bigcirc CH_2 - S \\ CH_2 - S \\ CH_2 - S \\ 1 \end{bmatrix} CO$$

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-

$$ClCH_2COCl \xrightarrow{H_2S} ClCH_2COSH \xrightarrow{KSH} HSCH_2COSH$$

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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		1,5 21111				
	$\begin{array}{ccc} \operatorname{RCHO} + \operatorname{HSCH}_2\operatorname{COSH} & \longrightarrow & \operatorname{RCH} \\ 3 & & & \\ 3 & & & \\ & & & \\ 3 & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$					
R	Yield, %	Bp, °C (mm)	Nmr (CCl4), 8	Element	Caled, %	Found, %
CH_3	27	85-86 (6)	4.95 (q, 1 H)	С	35.83	35.92
			3.71 (s, 2 H)	\mathbf{H}	4.51	4.55
			1.76 (d, 3 H)	\mathbf{s}	47.73	47.72
C_2H_5	29	86(2)	4.74 (t, 1 H)	\mathbf{C}	40.54	40.59
			3.63 (s, 2 H)	Η	5.44	5.40
			2.28-1.80 (m, 2 H)	\mathbf{s}	43.21	43.04
			1.10 (t, 3 H)			
n-C ₃ H ₇	42	96-99(2)	4.82 (t, 1 H)	С	44.44	44.56
			3.64 (s, 2 H)	н	6.22	6.09
			2.20-1.23 (m, 4 H)	\mathbf{S}	39.47	39.54
			0.98 (t, 3 H)			
$\rm C_6H_5$	31	141-143(2)	7.60-7.17 (m, 5 H)	\mathbf{C}	55.10	55.29
		(mp 50-51)	5.93 (s, 1 H)	\mathbf{H}	4.11	4.05
			3.74 (s, 2 H)	\mathbf{s}	32.62	32.71

TABLE I 1.3-DIMPTOLAN-4-ONE DEPINATIVES

diate, but attempts to isolate 5 resulted in failure. The structures of the products 2 were confirmed with the elemental analyses and nmr spectra presented in Table I. Identification of the products 4 was made by comparison of their physical properties with reported values.³

Experimental Section

1,3-Dithiolan-2-one (1).-To a solution of 1,2-ethanedithiol (9.4 g, 0.1 mol) and pyridine (15.8 g, 0.2 mol) in toluene (150 ml), phosgene (9.9 g, 0.1 mol) dissolved in 35 ml of toluene was added at 0°. The mixture was stirred for 3 hr at the same temperature, and precipitated pyridine hydrochloride was filtered off. The filtrate was washed (10% aqueous Na₂CO₃), dried (Na₂SO₄), and distilled. A fraction, bp 78-82° (4 mm), was collected, cooled, and recrystallized from n-hexane to give 1: mp 34-35° (lit. mp 34°);^{1,2} yield 8.1 g (67.5%); nmr (\tilde{CCl}_4) δ 3.69 (s).

Anal. Calcd for $C_3H_4OS_2$: C, 30.01; H, 3.36; S, 53.30. Found: C, 30.03; H, 3.32; S, 53.23.

Mercaptothioacetic Acid (3).-Hydrogen sulfide was passed into a mixture of chloroacetyl chloride (79 g, 0.7 mol) and anhydrous aluminum chloride (2.0 g) at 0° for 30 hr. The reaction mixture was filtered and the filtrate was distilled to obtain chlorothioacetic acid (56.2 g, 72.7%), bp 34-36° (5 mm).

A solution of KOH (90 g) in ethanol (90%, 270 ml) was saturated with H₂S at 0°, and chlorothioacetic acid (30 g, 0.27 mol) was added slowly at about -5° . After KCl was removed by precipitation, the filtrate was concentrated to about 100 ml, acidified with cold 3 N HCl, and extracted with ether. Distillation gave 3: bp 61-62° (8 mm); yield 24.6 g (84.5%); nmr (CCl₄) δ 5.18 (s, 1 H), 3.60 (d, 2 H), 2.37 (t, 1 H); ir bands at 2550, 1680 cm⁻¹.

Anal. Calcd for C₂H₄OS₂: C, 22.23; H, 3.73; S, 59.23. Found: C, 22.45; H, 3.77; S, 58.97.

1,3-Dithiolan-4-one (2).-To a solution of 3 (0.25 mol) and p-toluenesulfonic acid (0.5 g) in benzene (250 ml), aldehyde (0.5 mol) was added slowly at room temperature and stirred for 5 hr. The mixture was then refluxed for 10 hr, the water formed in the reaction being removed continuously by azeotropic distillation, washed (10% aqueous Na_2CO_3), dried (Na_2SO_4), and fractionally distilled to give two fractions and residual tar. The first fraction was the compound 4 (yield 5-15%); the second was redistilled to give 2 (Table I). The ir spectra of 2 showed strong absorption of C=O in the range of 1690-1685 cm⁻¹.

Registry No.—1, 2080-58-2; 2 (R = CH_3), 41755-28-6; 2 $(R = C_2H_3), 41755-29-7; 2 (R = n-C_3H_7), 41701-10-4; 2 (R = Ph), 41701-11-5; 3, 30298-36-3; acetaldehyde, 75-07-0; pro$ pionaldehyde, 123-38-6; butyraldehyde, 123-72-8; benzalde-hyde, 100-52-7.

Raney Nickel Catalyzed Decarbonylation of Formate Esters

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During investigation of a series of formate esters, we had occasion to study the effect of high-temperature treatment in the presence of Raney nickel (activity W2).¹ At reflux the esters were observed to undergo smooth decarbonylation to the corresponding alcohols. Subsequent dehydrogenation to the corresponding aldehydes or ketones also occurred under reaction conditions.²⁻⁵ Typical product distributions for a variety of formate esters are shown in Table I.

$$\begin{array}{c} O \\ RR'CHOCH \xrightarrow{\parallel} & \underset{reflux (>150^\circ)}{\overset{} \longrightarrow} \\ \end{array}$$

Little reaction was observed below 150°, with rates increasing as the boiling points of the higher formates were approached. As indicated in Table I, conversion of low-boiling esters (e.g., n-hexyl and cyclohexyl for-

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