Generation and Synthetic Applications of 2-Lithio-1,3-dithianes

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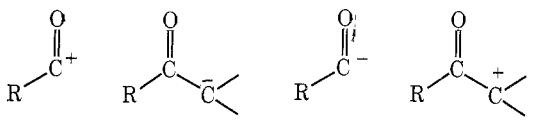
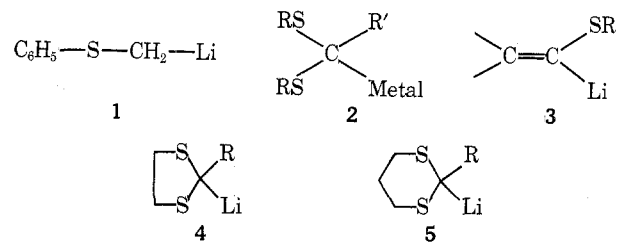
The preparation and metalation of 1,3-dithianes leads to protected acyllithium derivatives which are synthetically equivalent to acyl anions. Experimental procedures and a number of examples are given for the reactions of 2-lithio-1,3-dithianes with common electrophiles such as alkyl, allyl, and benzyl halides, aldehydes, ketones, and carboxylic acid derivates, as well as 1,2-and 1,3-oxides. The examples given demonstrate the high nucleophilicity of 2-lithio-1,3-dithianes and the value of these reagents in synthesis.

One of the major objectives of modern organic synthesis is the broadening of techniques for assembling collections of carbon atoms and functional groups. In order to increase the probability of developing simple routes for the synthesis of complex molecules, it is desirable to have reagents of opposite polarity for the introduction of a given fragment or synthon.[1] Thus, the nucleophilic cyanide, CN^-, or the electrophilic carbon dioxide, CO_2, can be used for incorporating the synthon COX into a molecule. We consider the design of new reagents which are the *equivalents* of inaccessible nucleophiles or electrophiles an effective strategy for the extension of the general methodology of organic synthesis.[1-5] Among the most commonly encountered reactive sites are carbonyl groups which, in their normal reactivity, provide acyl cation and enolate anion equivalents A and B, respectively. At the outset[2] of our work to be described here in detail,[6] there were no general methods supplying the counterparts, acyl anions C or enolate cations D.



A B C D

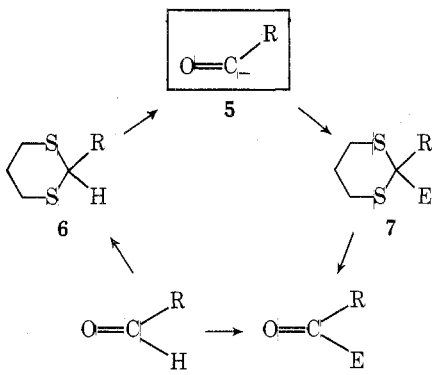
We thought that sulfur-stabilized anions might be suitable as masked nucleophilic acylating equivalents. Alkali metal derivatives of such anions had been generated previously by Gilman and Webb[7] and by Arens and Fröling[8] who showed that thioanisole could be metalated to give **1** and that certain thioacetals could be converted to compounds of type **2**. However, the yields were low, the experimental procedures unsatisfactory, and the structural limitations severe. In attempts to improve these reactions, we found[9] that solutions of **1** and **2**, R = C_6H_5, R′ = H, metal = Li, can be obtained quantitatively by metalation of corresponding precursors with butyllithium in tetrahydrofuran (THF). Likewise, a derivative **3** could be made under these conditions for the first time.[9] Both **2** and **3** are nucleophilic acylating reagents C, because by hydrolysis of their products with electrophiles, carbonyl compounds are formed in which a formerly electrophilic atom has been attached to the carbonyl carbon. While examining the scope and limitations of creating Li derivatives **2** and **3**[10] for this



1 **2** **3**

4 **5**

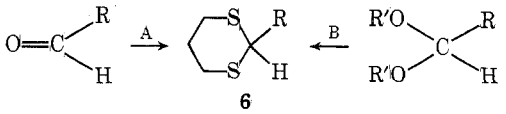
Scheme I



purpose, we also investigated the cyclic 2-lithio-1,3-dithiolanes (**4**) and -dithianes (**5**). The former underwent facile elimination to form ethylene and dithiocarbonate; the latter turned out to be most generally available and satisfactory. As indicated in Scheme I, these sulfur-stabilized anionic reagents are equivalent to acyl anions which implies that they can be used effectively to reverse the characteristic electrophilicity of a carbonyl carbon (symmetrization of reactivity,[1] reversible umpolung[5]). In the following sections we will discuss the preparation of 1,3-dithianes **6** from carbonyl derivatives, their metalation to give **5**, and the reactions of lithiodithianes **5** with various electrophiles to form products **7**. We have previously supplied full accounts of our work on the use of **5** for the preparation of silyl ketones[11a] and of cyclic ketones.[11b] Our contributions to the methods of hydrolysis of thioacetals have been published elsewhere.[11] We have also extensively summarized[3-5] actual examples of the synthesis of carbonyl compounds by the dithiane route and have reviewed[3,5] the many alternative reagents for nucleophilic acylation developed since our early preliminary publication.[2]

Preparation of 1,3-Dithianes and Conversion to 2-Lithio-1,3-dithianes (5)

Dithianes **6** are readily produced from aldehydes (method A) or acetals (method B) by standard methods.[12,13] We



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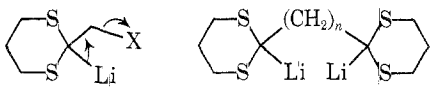
found the use of chloroform as a solvent and hydrogen chloride as catalyst most convenient in both cases. The products can be readily distilled or recrystallized. Their nmr spectra may show a very complex pattern from the protons in the 4, 5, and 6 positions of the ring.[4] The conversion of dithianes **6** into 2-lithiodithianes **5** is most conveniently achieved by adding an equimolar amount of *n*-

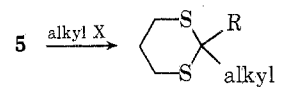
butyllithium to a THF solution of a dithiane at −20°. The reaction time varies with the steric and electronic character of the group R in the 2 position. Thus, with R = C_6H_5 metalation occurs within a few minutes, while the *tert*-butyl derivative requires about 5 hr for complete metalation. The progress of the reaction can be followed by sampling aliquots from the solution which are deuterated. The degree of deuterium incorporation is determined by nmr spectroscopy (see Experimental Section). Li derivatives of type **8** with a leaving group X (OR, SR, halogen, CN)[11b,14-16] cannot be generated under these conditions, dilithio compounds **9** are accessible if $n > 3$.



8 **9**

Alkylation of 2-Lithio-1,3-dithianes

This reaction converts the formaldehyde derivative **5**, R = H, into thioacetals of higher aldehydes, or thioacetals **5**, R ≠ H, into thioketals **10**. It proceeds extremely rapidly



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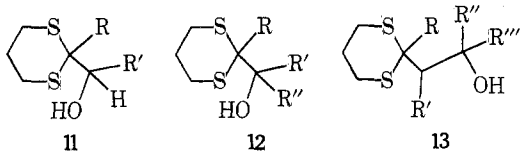
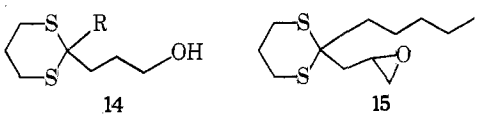
with primary alkyl iodides (15 min at −78°) and with allylic acid and benzylic halides. In other cases, longer periods of time are required (see Table II). In order to obtain good yields, the main side reaction, *i.e.*, elimination of HX from the halide, must be suppressed by carrying out the alkylations at low temperature. Work-up of samples from the reaction mixture, which sometimes precipitates lithium halide, is recommended to follow the progress of C–C formation. Tertiary and cyclic halides (cyclohexyl iodide), secondary chlorides, and primary and secondary tosylates could not be used successfully in these intermolecular alkylations.

Hydroxyalkylations of 5 with Aldehydes, Ketones, Oxiranes, and Oxetanes

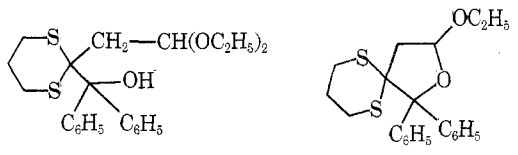
Carbonyl compounds and small-ring ethers react readily with lithiodithianes to give derivatives of α-, β-, and γ-hydroxy aldehydes or ketones of the general structures **11–14**.



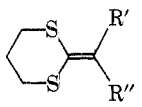
11 **12** **13**



14 **15**



16 **17**



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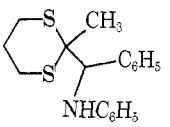
Aldehydes or ketones should be added to the solutions of **5** at −78° which minimizes possible enolization. Under these conditions, readily enolized ketones, such as cyclopentanone and cyclohexanone, give the products of carbonyl addition in high yields. This demonstrates the very effective nucleophilicity of the sulfur-substituted lithium reagents **5**. Epoxides and oxiranes are opened very slowly. However, high yields of derivatives **13** and **14** are obtained if the reaction mixtures are stored under an inert atmosphere in a refrigerator (0°) or freezer (−20°) for up to a week. (At higher temperatures, solutions of lithiodithianes in THF are not sufficiently stable.) Epichlorohydrin can be used for epoxyalkylations; *cf.* **5** → **15**.

The adduct **16** of 2-lithio-2-(β,β-diethoxyethyl)-1,3-dithiane to benzophenone could not be isolated; instead the product was the cyclic acetal **17**. Other ketone and aldehyde adducts **11** and **12** with R = H can be dehydrated directly or through the chlorides derived from these alcohols to give ketene thioketals **18**.[17]

(Table III in the Experimental Section lists a number of products **11–14** obtained, together with the yields and physical and spectroscopic data.) The carbonyl addition of lithiodithianes **5** is, of course, also applicable to carbonyl analogs. For instance, the amino ketone derivative **19** is formed quantitatively from methyldithiane and benzalanilide.



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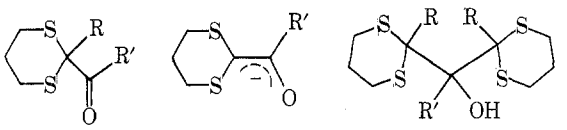
Acylations of Lithiodithianes

This reaction leads to derivatives of 1,2-dicarbonyl compound (**20**) in which one of the carbonyl groups is protected



20 **21** **22**

as a thioacetal. Of the potential acylating reagents, enolizable tertiary carboxamides and nitriles cannot be used since they are converted to enolates.[18] Esters and acid chlorides can be employed with the following limitations: (a) if unsubstituted lithiodithiane is to be acylated, the primary product **20**, R = H, contains a relatively acidic proton in the dithiane 2 position which is abstracted by excess lithium reagent to give **21**, resulting in a 2:1 stoichiometry of the acylation; (b) if R in **20** is not hydrogen, a second mole of lithiodithiane can attack as a nucleophile to give the diadduct **22**. Therefore, the lithiodithiane should be added to a large excess of acylating reagent. Finally, those nonenolizable acylating derivatives which do not lead to free carbonyl compounds **20** until the aqueous work-up of the original reaction mixture, such as carbon dioxide (RCOOLi → **20**, R′ = OH), dimethylformamide (RCH[N(CH_3)$_2$]OLi → **20**, R′ = H), and aromatic nitriles (R_2C=NLi → **20**, R′ = aryl) furnish acyldithianes in excellent yields. Examples for each of these different types of acylations are given in the Experimental Section.

Experimental Section

Flasks and stirring bars used for the generation and reactions of lithiodithianes were dried for *ca.* 12 hr at 120° and allowed to cool in a desiccator over P_4O_{10}. Distillations were carried out under nitrogen. Anhydrous THF was obtained by distillation from LAH. The yields listed in the tables were determined by concentration of aliquots and nmr analysis.

Most boiling points given correspond to bath temperatures measured during short-path evaporative distillation. Melting points are uncorrected. Chemical shifts are given in τ values relative to

Table I
Rates of Metalation of 1,3-Dithianes at −20°

R in 2 position of 1,3-dithiane	Reaction time with *n*-butyllithium before hydrolysis with D_2O, hr	Recovery of dithiane, %	Deuteration, %
H	1.3	95	>95
CH_3	0.6	77 (volatile)	80
	1.2	69	>95
n-C_5H_{11}	0.8	80	85
$CH_2CH(OC_2H_5)_2$	1.7	86	>95
i-C_3H_7	1.6	96	>95
t-C_4H_9	1.3	90	80
	15.0	85	>95

internal tetramethylsilane. Infrared absorption data are given in microns and do not include the band at 11.00 ± 0.05 μ typical of 1,3-dithianes.

A. **General Procedure for the Preparation of 1,3-Dithianes (6) from Aldehydes or Their Acetals (Method A and B).** A 0.1–1 *M* solution of an aldehyde or acetal in chloroform is combined with an equimolar amount of propane-1,3-dithiol at room temperature. With aldehydes, the solution is kept for 1 hr prior to cooling to −20°; with acetals, the solution is cooled in an ice bath immediately after mixing the components. Dry HCl gas is slowly passed through the solution for 5–10 min, or alternatively, a 0.05–0.10 *M* amount of BF_3 etherate or $ZnCl_2$ can be added. The solutions are allowed to warm to room temperature. Reaction mixtures from aldehydes are worked up after 1–15 hr by successively washing three times each with water, 10% aqueous KOH, and water and drying over K_2CO_3. Evaporation of the solvent furnishes crude products which are distilled or recrystallized. The forerun of distillations is often yellow and, although seemingly pure by nmr analysis, is not satisfactory for conversion to lithiodithianes.

Ketones or ketals can be converted to disubstituted dithianes similarly. We have previously given specific procedures for the preparation of 1,3-dithiane,[19] 2-methyl-,[11c] 2-chloromethyl-,[20] 2-(β-chloroethyl)-,[11b] 2-*sec*-butyl-,[21] 2-phenyl-1,3-dithiane,[22] and of the bis(1,3-propylene)dithioacetals of malonaldehyde and succinaldehyde.[11b] Five more examples are described below.

2-Ethyl-1,3-dithiane (6, R = C_2H_5). From 0.3 mol of propionaldehyde an 87% yield of distilled dithiane was obtained: bp 91° (10 mm) (lit.[12] 85° (5 mm), 112° (21 mm)); $n^{25}D$ 1.5501; ir (neat) 3.4, 6.88, 7.04, 7.85, 8.42, 9.10, 12.0, 12.4, 13.1, and 14.6 μ; nmr (CCl_4) 8.96 (t, *J* = 6.3 Hz, CH_3), 6.08 (t, *J* = 6.7 Hz, 2-dithiane H). *Anal.* Calcd for $C_6H_{12}S_2$: C, 48.64; H, 8.16; S, 43.20. Found: C, 48.63; H, 7.99; S, 43.43.

2-*n*-Pentyl-1,3-dithiane (6, R = *n*-C_5H_{11}). On a 0.125 molar scale a 68% yield was obtained from hexanal: bp 85° (0.35 mm); $n^{30}D$ 1.5247; ir (neat) 3.86, 6.85, 7.04, 7.85, and 8.5 μ; nmr (CCl_4) 6.04 (degenerate t, *J* = 6.5 Hz, 2-dithiane H). *Anal.* Calcd for $C_9H_{18}S_2$: C, 56.82; H, 9.54; S, 33.64. Found: C, 56.90; H, 9.42; S, 33.63.

2-*tert*-Butyl-1,3-dithiane (6, R = *t*-C_4H_9). From 0.016 mol of pivalaldehyde an 82% yield of dithiane was obtained: bp 61° (0.4 mm) (lit.[12] 129° (22 mm)); mp 35.5–36.0° (methanol); ir (CCl_4) 3.32, 3.40, 6.78, 6.83, 7.04, 7.18, 7.31, 7.82, 8.04, 8.10, 8.67, 9.71, 10.81, 11.53, and 14.6 μ; nmr (CCl_4) 8.93 (s, *t*-C_4H_9), 6.12 (s, 2-dithiane H). *Anal.* Calcd for $C_8H_{16}S_2$: C, 54.53; H, 9.15; S, 36.32. Found: C, 54.46; H, 9.05; S, 36.14.

Bis(1,3-propylene)dithioacetal of Methyl Glyoxal. 2-Formyl-2-methyl-1,3-dithiane (see below, acylation products) was converted in 77% yield to the bis(dithiane) derivative: mp 115.2–115.7° (methanol); ir ($CHCl_3$) 3.28, 3.37, 3.47, 6.93, 7.05, 7.27, 7.83, 8.50, and 11.50 μ; nmr ($CDCl_3$) 8.20 (s, CH_3), 5.26 (s, 2-dithiane H). *Anal.* Calcd for $C_9H_{16}S_4$: C, 42.86; H, 6.39; S, 50.75. Found: C, 42.86; H, 6.31; S, 50.74.

2-(Cyclohexen-1-yl-4)-1,3-dithiane. Using $ZnCl_2$ as catalyst 100 mmol of the aldehyde gave 6.3 g (31%) of dithiane: bp 104° (0.19 mm); nmr (CCl_4) 7.7–8.5 (9 H multiplet), 5.95 (d, 2-dithiane H), 4.4 (2 H multiplets).

B. **General Procedure for the Preparation of 2-Lithio-1,3-dithiane (5) Solutions in THF.** A round-bottomed flask with ST neck and side arm is equipped with a magnetic spin bar, a three-way stopcock, and a serum cap. Solid dithianes are weighed into the flask prior to subsequent flushing with nitrogen or argon. The reaction vessel is kept under positive inert gas pressure until work-up. Solvents, liquid reagents, and solutions of reagents are introduced, and samples are withdrawn through the serum cap by hypodermic syringes. To avoid loss of pressure, pierced caps are sealed with parafilm tape.

The amount of freshly distilled THF necessary to obtain a 0.1–0.5 *M* solution of dithiane is added. A 5% excess of *n*-butyllithium in *n*-hexane (1.5–2.5 *M*) is added at a rate of 3–5 ml/min to the solution stirred at −40°. After 1.5–2.5 hr at −25 to −15°, most dithianes are metalated quantitatively (Table I) as determined by deuteration of an aliquot of the solution containing 50–100 mg of dithiane. This is done by injecting the withdrawn solution into 1–3 ml of D_2O in a small separatory funnel and extracting with ether, methylene chloride, or pentane; the organic layer is dried for a few minutes with K_2CO_3 and concentrated evaporatively. Integration of the dithiane C_2-proton nmr signal *vs.* any other well-defined and separated peak of the particular dithiane thus provides the extent of deuteration with an accuracy of ±5% within 15 min. Examples of large scale deuteration for the preparation of deuterioaldehydes have been described in detail.[22,23]

The anion solutions are clear and colorless if R is H or alkyl, orange if R is phenyl. The solution of dithiane **5**, R = H, can be stored for a few hours at room temperature without decomposition. After 2 weeks at −25° the solutions of **5**, R = H, CH_3, C_2H_5, showed no decomposition; with R = *t*-C_4H_9, however, 5% decomposition was detected after 17 hr under these conditions.

Instead of *n*-butyllithium, the *tert*-butyl derivative can be used to metalate dithianes at lower temperatures or within shorter periods of time.

Detailed procedures for the preparation of lithiodithianes have been published previously: **5**, R = H,[24] R = CH_3,[25] R = C_6H_5.[22]

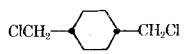
C. **General Procedure for the Alkylation of 2-Lithio-1,3-dithianes with Primary and Secondary Halides to Give 10.** At −60 to −78° an equivalent of neat halide is added to a stirred solution of 2-lithio-1,3-dithiane. With primary iodides, allylic, and benzylic halides the reaction takes place within a few hours at this temperature. In the case of secondary iodides and especially bromides and primary chlorides, the reaction mixture should be kept between −20 to −60° for up to 5 days, because too rapid warming leads to appriciable elimination. The progress of the reactions should be checked by withdrawing small samples, hydrolyzing, and analyzing by nmr. Nonactivated secondary chlorides and primary and secondary tosylates are not useful alkylating reagents.

Before work-up the solutions from which lithium halide or products may crystallize are allowed to slowly warm to 0° and are kept in a refrigerator for up to 3 days. The mixture is poured into three volumes of water; large-scale preparations are concentrated evaporatively prior to hydrolysis to avoid inconvenient manipulation with large separatory funnels. Several extractions with chloroform or pentane furnish an organic solution which is washed twice each with water, 7% aqueous KOH, and again water and dried over K_2CO_3. The residue obtained after solvent removal is distilled *in vacuo* or recrystallized. Specific procedures have been given by us[2,11,17,21,22,24,26] previously, including cases in which two identical or two different alkyl groups have been introduced by sequential one-pot alkylations starting from unsubstituted dithiane. Table II lists some of the reactions carried out.

D. **Hydroxyalkylations with Carbonyl Derivatives, Oxiranes, and Oxetane. (a) (1) General Procedure for the Reaction of 5 with Carbonyl Compounds to Give Alcohols 11 and 12.** A neat liquid carbonyl compound or the THF solution of a solid carbonyl compound is added to the vigorously stirred solution of the anion at −70°. In large-scale reactions the addition rate should be adjusted so that the temperature of the reaction mixture does not exceed −50°. Many reactions of this type can also be carried out at higher temperatures (up to −20°); however, the tendency of the highly nucleophilic lithiodithianes to abstract protons from enolizable carbonyls decreases with decreasing temperature. With aldehydes the reaction is completed instantaneously. With highly hindered or otherwise unreactive ketones, *e.g.*, benzophenone, and/or with lithiodithianes bearing bulky 2 substituents, subsequent storage of the reaction mixture at −20° (enolizable ketones) or at 0° (benzophenone) for 12–24 hr is favorable. The work-up method described in the general alkylation procedure is followed using methylene chloride or chloroform as solvent.

For examples, see Table III; a detailed procedure for the reaction of **5**, R = CH_3, with cyclohexanone has been published.[25]

Table II
Products 10 of Alkylation of 2-Lithio-1,3-dithianes 5

5, R	Registry No.	Halide, R¹–X	Registry No.	Product, –1,3-dithiane [a]	Registry No.	Reaction times, hr (°C)	Yield, %	mp (°C), bp (°C (mm)), n_D °C
H	36049-90-8	CH_3I	74-88-4	2-Methyl-	6007-26-7	3 (0)	86	94 (21), 1.5573^{25}
H		C_2H_5I	75-03-6	2-Ethyl-	6007-23-4	4 (0)	85	116 (22), 1.5480^{25}
H		n-$C_5H_{11}Br$	110-53-2	2-n-Pentyl-	21777-32-2	13 (0)	92	1.5209^{28}
H		CH_3CHICH_3	75-30-9	2-Isopropyl-	6007-25-6	14 (0)	82	52 (0.9) (lit.[13] 134 (35)),
		$CH_3CHBrCH_3$	75-26-3			19 (0)	68	1.5410^{28}
H		p-tol-$O(CH_2)_5Br$	53178-42-0	2-[(ω-p-Tolyloxy)-n-pentyl]-	53178-43-1	1 (–30) 12 (0)	88	65.1–65.7
H		$ClCH_2CH(CH_3)CH_2Br$	6974-77-2	2-(3-Chloro-2-methylpropyl-1)-	53198-70-2	1 (–50) 12 (–20)	81	105 (0.08), 1.5555^{20}
H			53188-14-0	2-(*cis*-4-Chloromethylcyclohexylmethyl)-	53178-44-2	24 (–20) 23 (0)	73	136 (0.07), 1.5622^{25}
H		$(C_2H_5O)_2CHCH_2Br$	2032-35-1	2-(2,2-Diethoxyethyl-1)-	5849-13-8	46 (0)	87	115 (0.3), 1.5099^{26}
H		$\frac{1}{2}Br(CH_2)_3Br$	109-64-8	Bis(1,3-propylene)dithioacetal of glutaraldehyde	4883-05-0	2 (–30) 22 (0)	93	101.5–102.0 (CH_3OH)
H		$\frac{1}{2}Br(CH_2)_4Br$	110-52-1	Bis(1,3-propylene)dithioacetal of adipaldehyde	4883-04-9	0.5 (–50) 21 (0)	96	102.5–103.5 (pentane–cyclohexane)
CH_3	27969-97-7	CH_3CHICH_3		2-Methyl-2-isopropyl-	5849-02-5	0.5 (–60) 8 (0)	83	60 (0.3), 1.5403^{25}
CH_3		$C_6H_5CH_2Br$	100-39-0	2-Methyl-2-benzyl-	5849-03-6	0.5 (–70) 75 (0)	98	113 (0.08), 1.5966^{28}
CH_3		$\frac{1}{2}Br(CH_2)_4Br$		Bis(1,3-propylene)dithioacetal of octane-2,7-dione	5012-00-0	0.5 (–70) 76 (0)	89	108.5–109.0 (pentane–cyclohexane)
C_2H_5	53178-38-4	$(CH_3)_2C{=}CHCH_2Br$	870-63-3	2-Ethyl-2-(3′,3′-dimethylpropen-2′-yl-1′)-	53178-45-3	0.5 (–60) 12 (0)	71	85 (0.03), 1.5438^{25}
$CH(CH_3)_2$	53178-39-5	CH_3CHICH_3		2,2-Diisopropyl-	5849-29-6	0.5 (–5) 14 (0)	80	95 (0.5), 1.5392^{25}
t-C_4H_9	53178-40-8	CH_3CHICH_3		2-Isopropyl-2-*tert*-butyl-	5849-05-8	40 (0)	50	
n-C_5H_{11}	21777-36-6	CH_3CHICH_3		2-n-Pentyl-2-isopropyl-	5849-10-5	12 (0)	85	84 (0.03), 1.5245^{24}
n-C_5H_{11}		n-$C_5H_{11}Br$		2,2-Di-n-pentyl-	5849-09-2	45 (0)	83	118 (0.35), 1.5117^{25}
C_6H_5	53178-41-9	CH_3CHICH_3		2-Isopropyl-2-phenyl-	5849-12-7	14 (0)	97	50.5–51.5 (CH_3OH)

[a] Satisfactory C, H, and S analyses were obtained.

Table III
α-, β-, and γ-Hydroxyalkylated Dithianes 11–14 from 5 and Aldehyde, Ketones, Epoxides, and Oxetane (See General Procedures Da1 and Db1)

5, R	Electrophile	Registry No.	Product, -1,3-dithiane[a]	Registry No.	Yield, %	mp (°C) bp (°C (mm)), n_D °C
H	Benzaldehyde	100-52-7	2-(Phenylhydroxymethyl)- (11)	5849-19-4	99	71.3–72.1 (pentane–cyclohexane–benzene)
H	Cyclopentanone	120-92-3	2-(1'-Hydroxycyclopentyl-1')- (12)	5849-20-7	70	113 (0.02), 1.5755^{25}
H	Cyclohexanone	108-94-1	2-(1'-Hydroxycyclohexyl-1')- (12)	5849-22-9	95	
CH_3	Cyclohexanone		2-Methyl-2-(1'-hydroxycyclohexyl-1')- (12)	5849-24-1	86	165 (1.2), 1.5723^{23}
H	Cyclohexanone		2-(1'-hydroxycyclohexen-2'-yl-1')- (12)	53178-46-4	77	Oil, chromatography over silica–gel
H	Benzophenone	119-61-9	2-(Diphenylhydroxymethyl)- (12)	5849-23-0	98	136.0–136.5 (pentane–cyclohexane, 1:3)
CH_3	Benzophenone		2-Methyl-2-(diphenylhydroxymethyl)- (12)	5849-25-2	98	136.5–137.5 (methanol)
C_2H_5	Benzophenone		2-Ethyl-2-(diphenylhydroxymethyl)- (12)	53178-51-1	99	97.5–98.0 (methanol)
$CH(CH_3)_2$	Benzophenone		2-Isopropyl-2-(diphenylhydroxymethyl)- (12)	5849-27-4	70	152.5–153.0 (methanol)
n-C_5H_{11}	Benzophenone		2-n-Pentyl-2-(diphenylhydroxymethyl)- (12)	5849-26-3	98	94.5–95.5 (methanol)
n-C_5H_{11}	Propylene oxide	75-56-9	2-n-Pentyl-2-(β-hydroxypropyl)- (13)	53178-52-2	95	140 (0.15), 1.5300^{20}
H	Styrene oxide	96-09-3	2-(β-hydroxy-β-phenylethyl)- (13)	53178-47-5	87	Oil
CH_3	Styrene oxide		2-Methyl-2-(β-hydroxy-β-phenylethyl)- (13)	5849-17-2	78[b]	Oil
H	Oxetane	503-30-0	2-(3'-Hydroxypropyl)- (14)	53178-48-6	80[c]	120 (0.03), 1.5660^{20}

[a] Satisfactory C, H, and S analyses were obtained. [b] The product was hydrolyzed under neutral conditions ($HgCl_2$-HgO-CH_3OH), and the crude hydroxyaldehyde isolated was added to a sulfuric acid–ethanol 2,4-dinitrophenylhydrazine reagent solution. The DNP of cinnamaldehyde precipitated in 76% yield and had the melting point given in the literature, 253–254° (from acetic acid). [c] Hydrolysis as described in footnote b gave 55% of the DNP of benzylidene acetone, mp 156.0–156.5° (ethanol).

For the conversion of the adducts of unsubstituted dithiane to benzaldehyde, benzophenone, and cyclohexanone into ketene thioacetals **18**, see sections a2 and a3; the preparation of the products **17** and **19** is described in sections a4 and a5, respectively.

(2) 1,3-Propylenedithioketals of the Ketenes of Phenyl- and Diphenylacetic Acid (18, R' = C_6H_5, R'' = H, and 18, R' = R'' = C_6H_5). In a round-bottomed flask, equipped with a water separatory head, a solution in benzene which is 0.05 *M* in carbinol and 0.0005–0.005 *M* in *p*-toluenesulfonic acid monohydrate is stirred and heated at reflux. (In large-scale reactions the concentrations can be increased.) Depending on the particular carbinol and on the scale used, the water separation is over in 3–20 min. The solution is allowed to cool to room temperature, washed with 10% KOH and with water, and dried over K_2CO_3. Evaporation of the solvent furnishes the dehydrated product in nearly quantitative yield.

18, R' = C_6H_5, R'' = H: yield 93%; bp 150° (0.14 mm); ir (neat) 3.25, 3.40, 3.50, 6.30, 6.53, 6.73, 7.11, 7.72, 11.53, 12.35, 13.4, and 14.4 μ; nmr (CCl_4) 4.00 (s, vinylic H), 2.75 (m, C_6H_5). *Anal.* Calcd for $C_{11}H_{12}S_2$: C, 63.45; H, 5.81; S, 30.74. Found: C, 63.36; H, 5.79; S, 30.40. **18**, R' = R'' = C_6H_5: yield 97%; mp 134.5–135.0 (pentane); ir ($CHCl_3$) 3.20, 3.25, 3.35, 6.25, 6.70, 6.93, 7.05, 7.68, 9.39, 9.68, 11.6, and 14.24 μ; nmr ($CDCl_3$) 2.75 (broad s, C_6H_5). *Anal.* Calcd for $C_{17}H_{16}S_2$: C, 71.82; H, 5.67; S, 22.51. Found: C, 71.66; H, 5.64; S, 22.43.

(3) 2-Cyclohexylidene-1,3-dithiane (18, R'–R'' = $(CH_2)_5$). Pure 2-(1-hydroxycyclohexyl-1)-1,3-dithiane (5.64 mmol, 1.230 g) and 5.2 g of pyridine were dissolved in 100 ml of CH_2Cl_2 and stirred in an ice bath. Thionyl chloride (24.8 mmol, 2.95 g) was added all at once. The solution turned yellow, was stirred for 25 min at 0° and for an additional 10 min after removal of the bath, and was poured on ice. The aqueous layer was extracted twice with CH_2Cl_2, and the combined organic layers were washed successively three times each with water, saturated $CuSO_4$, and water. Drying over Na_2SO_4 and evaporating the solvent gave 1.161 g (86.5%) of colorless crystals of 2-(1-chlorocyclohexyl-1)-1,3-dithiane, mp 95.6–96.5° (methanol): molecular ion in mass spectrum at 236; ir ($CHCl_3$) 3.40, 6.95, 7.10, and 7.90 μ; nmr ($CDCl_3$) 5.66 (s, 2-dithiane H). *Anal.* Calcd for $C_{10}H_{17}ClS_2$: C, 50.77; H, 7.24; S, 27.08. Found: C, 50.72; H, 7.15; S, 27.36.

A solution of 1.774 g of the chloride in 40 ml of dry THF was added within 5 min to a suspension of 1.105 g of potassium *tert*-butoxide (9.75 mmol) in 5 ml of THF stirred in an ice bath. The mixture turned orange, the temperature was allowed to rise to 20° within 1 hr, and stirring was continued at room temperature for 14 hr to give a brown, pale solution. Work-up with chloroform led to the isolation of 1.398 g (93%) of light brown crystals of **18**, R'–R'' = $(CH_2)_5$: mp 93.6–94.0° (methanol); ir ($CHCl_3$) 3.35, 3.45, 6.32, 6.91, 7.02, 7.83, 10.05, 11.50, and 12.22 μ; *Anal.* Calcd for $C_{10}H_{16}S_2$: C, 59.98; H, 8.05; S, 31.96. Found: C, 60.14; H, 8.01; S, 32.05.

(4) 1,3-Propylenedithioketal of 2-Ethoxy-4-oxo-5,5-diphenyltetrahydrofuran (17). The solution of 10 mmol of 2-lithio-2-(β,β-diethoxyethyl)-1,3-dithiane is combined at −78° with an equimolar amount of benzophenone in THF. The temperature is allowed to rise to 0° within 3 hr, and the flask is sealed and stored in a refrigerator for 18 hr. Work-up with chloroform gives 95% of almost pure product which is recrystallized from a 6:2:1 mixture of pentane–cyclohexane–benzene to give 83% of analytically pure massive prisms: mp 144.0–145.2°; ir ($CHCl_3$) 6.72, 6.93, 8.9, 9.8,

10.0, and 11.29 μ; nmr ($CDCl_3$) 8.63 (t, J = 7.0 Hz, ethyl CH_3), 4.39 (d of d, J = 7.0 and 5.0 Hz, CH), 2.76 and 2.15 (aromatic protons as two multiplets), ratio 3:1:10. *Anal.* Calcd for $C_{21}H_{24}O_2S_2$: C, 67.73; H, 6.50; S, 17.18. Found: C, 67.49; H, 6.54; S, 17.03.

(5) *N*-Phenyl-2-phenylaminomethyl-2-methyl-1,3-dithiane (19) from 5, R = CH_3, and Benzalanilide. After combining equimolar amounts of the reactants, both dissolved in THF, at 0° on a 5 m*M* scale, the cooling bath was removed. After 1.5 hr the solution was poured into three times its volume of water. Extraction with chloroform yielded 98% of amine: mp 102.5–103.8° (methanol); ir ($CHCl_3$) 2.90, 2.95, 3.25, 3.30, 3.40, 3.50, 6.23, 6.68, 6.91, 7.04, 7.53, 7.92, 14.25, and 14.45 μ; nmr ($CDCl_3$) 8.46 (s, CH_3), 5.47 (s, CH), 5.10 (broad s, NH). *Anal.* Calcd for $C_{18}H_{21}NS_2$: C, 68.55; H, 6.71; N, 4.44; S, 20.29. Found: C, 68.19; H, 6.78; N, 4.49; S, 20.63.

(b) (1) General Procedure for Reactions of 5 with Oxiranes and Oxetanes. The neat three- or four-membered cyclic ether is added to the lithiodithiane solution stirred at −20°. The reaction vessel is closed under positive inert gas pressure and stored for up to 1 week in a refrigerator (0–5°) or a freezer (−20 to −30°). The work-up procedure is the same as described for the reactions with ketones (see above, Da1).

The reactions of 2-lithio-1,3-dithiane with ethylene, propylene, and cyclohexene oxide have been described in detail.[11b] Further applications of this general reaction are listed in Table III.

(2) Epoxide of 2-*n*-pentyl-2-(propen-2′-yl-1′)-1,3-dithiane Oxide (15) from 5, R = *n*-C_5H_{11}, and Epichlorohydrin. A solution of 2.506 g (27.1 mmol) of epichlorohydrin in 14 ml of THF was added to 26.9 mmol of 2-lithio-2-*n*-pentyl-1,3-dithiane at −70°. After storage at 0° for 24 hr, the mixture was worked up with water and CH_2Cl_2. Crude yield 94%, after distillation through a 10-cm column 3.50 g (64%) of a colorless oil was obtained: bp 123–125° (0.1 mm); n^{20}D 1.5326; ir (neat) 7.87, 11.80, 13.10 μ; nmr (CCl_4) typical terminal epoxide hydrogens as doublet of doublets at τ 7.63 (J = 4.2 and 5.7 Hz). *Anal.* Calcd for $C_{12}H_{22}OS_2$: C, 58.51; H, 9.00; O, 6.49; S, 26.00. Found: C, 58.49; H, 8.78; O, 6.52; S, 26.03.

E. **Reactions of 5 with Acylating Reagents. (a) Carboxylations, Preparation of 1,3-Dithiane-2-carboxylic Acids, 20, R′ = OH.** In a separatory funnel freshly chopped Dry Ice is added to 10 ml of THF and treated with a solution containing 5–10 mmol of a lithiodithiane which is injected by syringe. After warming to room temperature 50 ml of ether and 10 ml of 10% KOH are added. The organic layer is extracted twice with 5 ml of the KOH solution, and the combined alkaline layers are washed three times each with ether and chloroform, cooled in an ice bath, and acidified with stirring by dropwise addition of concentrated HCl. The acids are extracted into chloroform. Drying over Na_2SO_4 and solvent removal furnishes the crude products.

The yields of acids given below for three specific examples can be increased to nearly 100% by working under anhydrous conditions.

(1) 1,3-Dithiane-2-carboxylic Acid (20, R = H, R′ = OH). From 5 mmol of anion solution a 32% yield of acid was obtained: mp 114.5–116.0° (pentane–benzene) (lit.[27] 115–116°); ir ($CHCl_3$) broad absorption between 2.7 and 4.5 μ, 5.84, 7.08, 7.73, 8.04, 8.49, 9.90, 11.29, 12.20, and 14.53 μ; nmr ($CDCl_3$) 5.85 (s, 2-dithiane H), −0.42 (broad s, COOH).

(2) 2-Methyl-1,3-dithiane-2-carboxylic Acid (20, R = CH_3, R′ = OH). On a 3.4 m*M* scale a 70% yield was achieved: mp 133.5–135.0° (water); ir ($CHCl_3$) 2.7–4.4, 5.87, 6.89, 7.28, 7.85, 8.98, 9.25, 11.55, 12.4, and 14.3 μ; nmr ($CDCl_3$) 8.34 (s, CH_3); −1.86 (s, COOH). *Anal.* Calcd for $C_6H_{10}O_2S_2$: C, 40.91; H, 5.48; O, 18.17; S, 36.34. Found: C, 40.43; H, 5.67; O, 18.24; S, 36.16.

(3) 2-*tert*-Butyl-1,3-dithiane-2-carboxylic Acid (20, R = *t*-C_4H_9, R′ = OH). From 25 mmol of **5**, R = *t*-C_4H_9, 76% of the acid was isolated: mp 98.5–99.3° (pentane); ir ($CHCl_3$) 2.7–4.2, 5.70, 5.89, 7.05, 7.16, 7.31, 7.96, 12.25, and 14.3 μ; nmr ($CDCl_3$) 8.72 (s, CH_3), −0.83 (s, COOH). *Anal.* Calcd for $C_9H_{16}O_2S_2$: C, 49.08; H, 7.32; S, 29.06. Found: C, 49.02; H, 7.36; S, 28.85.

(b) Bis(1,3-propylenedithioacetals) 22 of 2-Hydroxy-1,3-dicarbonyl Compounds, 2-Formyl- (20, R′ = H) and 2-Acyl-1,3-dithianes 20, R′ ≠ H, by Reaction of 5 with Esters, Acid Chlorides, and Dimethylformamide.[28] (1) Ethyl-1,3-dithiane-2-carboxylate (20, R = H, R′ = OC_2H_5) from 5, R = H, and Ethyl Chloroformate. A solution of 29.1 mmol of 2-lithio-1,3-dithiane is stirred at −78° and combined with 1.64 g (15.2 mmol) of neat ethyl chloroformate. After raising the temperature to +20° within 2 hr the mixture was stirred for 4 hr and poured into water. Extraction with ether gave an organic layer which was washed with 10% KOH and dried over Na_2SO_4. Solvent evaporation furnished 4.23 g of crude product consisting of a 1:1 molar mixture of 1,3-dithiane and the desired ester, by nmr analysis. The former was removed evaporatively at 60° (0.6 mm), the ester distilled at 96° (0.4 mm): yield 2.22 g (76% calcd from chloroformate); n^{25}D 1.5385; ir (neat) 3.38, 5.77, 7.06, 7.36, 7.80, 8.78, and 9.74 μ; nmr (CCl_4) 5.98 (s, 2-dithiane H), 5.84 (q, J = 7.0 Hz, ethyl CH_2), 8.71 (t, J = 7.0 Hz, ethyl CH_3). *Anal.* Calcd for $C_7H_{12}O_2S_2$: C, 43.75; H, 6.29. Found: C, 43.99; H, 6.37.

(2) 2-Cinnamoyl-1,3-dithiane (20, R = H, R′ = Styryl) and Bis(1,3-propylenedithioacetal) of 2-Hydroxy-2-ω-styrylmalonaldehyde (22, R = H, R′ = Styryl) from 5, R = H, and Ethyl Cinnamate. The anion solution obtained from 1.0 g (8.3 mmol) of 1,3-dithiane was added within 5 min to 0.76 g (4.3 mmol) of ethylcinnamate dissolved in 5 ml of THF and stirred at −78°. Warming up and working up as described above (b1) give 1.30 g of a yellow oil which contains according to its nmr spectrum 42% of 1,3-dithiane, 42% of the ketone, and 16% of the alcohol. The alcohol is separated by adding 5 ml of ether and allowing the mixture to crystallize overnight; the ketone is recovered from the mother liquor by evaporation of the solvent and of 1.3-dithiane.

Alcohol (**22**): mp 176.6–177.4° (colorless, short, heavy prisms from methanol); ir ($CHCl_3$) 2.87, 3.27, 3.38, 3.99, 7.02, 7.83, 9.04, 9.34, 10.30, and 14.44 μ; nmr ($CDCl_3$) 5.38 (s, 2-dithiane H), 6.82 (s, OH), 3.12 and 3.77 (d, J = 16.0 Hz, vinylic hydrogens), 2.66 (m, C_6H_5). *Anal.* Calcd for $C_{17}H_{22}OS_4$: C, 55.13, H, 5.99; O, 4.32; S, 34.56. Found: C, 55.05; H, 6.03; O, 4.34; S, 34.45. Ketone (**20**): mp 99.5–100.0° (yellow, flat clustered needles from pentane–hexane–benzene 5:2:1); ir ($CHCl_3$) 3.28, 3.40, 3.50, 5.92, 6.01, 6.20, 6.33, 6.92, 7.03, 7.52, 9.33, 10.20, 11.14, 11.25, and 14.55 μ; nmr ($CDCl_3$) 5.46 (s, 2-dithiane H), 2.49 and 3.13 (d, J = 16.2 Hz, vinylic hydrogens), 2.6 (m, C_6H_5). *Anal.* Calcd for $C_{13}H_{14}OS_2$: C, 62.39; H, 5.64; O, 6.39; S, 25.58. Found: C, 62.70; H, 5.72; O, 6.23; S, 25.11.

(3) 2-Formyl-2-methyl-1,3-dithiane (20, R = CH_3, R′ = H) from 5, R = CH_3, and DMF. A 5% solution of DMF (0.81 g, 11.0 mmol) in THF was stirred at −5°; 10 mmol of the lithiodithiane were added and allowed to react for 15 hr in a refrigerator (−2°). Work-up with ether gave 1.12 g of a colorless liquid which contained 80% of the aldehyde (corresponding to 57% yield). The yield can be increased considerably using excess DMF freshly distilled from CaH_2 and lower temperatures: bp 63° (0.06 mm); n^{26}D 1.5612; ir (neat) 3.35, 3.30, 3.66, 5.79, 6.92, 7.01, 7.32, 7.80, 9.28, and 11.45 μ; nmr (CCl_4) 8.56 (s, CH_3), 1.00 (s, formyl H). *Anal.* Calcd for $C_6H_{10}OS_2$: C, 44.44; H, 6.22; O, 9.87; S, 39.47. Found: C, 44.48; H, 6.32; O, 10.15; S, 39.45. 2,4-Dinitrophenylhydrazone: mp 167.5–168.5 (yellow needles from ethanol); *Anal.* Calcd for $C_{12}H_{14}N_4O_4S_2$: C, 42.11; H, 4.12; N, 16.37. Found: C, 42.26; H, 4.24; N, 16.24. Conversion into bis(1,3-propylenedithioacetal) of methylglyoxal, see section A.

(4) Ethyl 2-Methyl-1,3-dithiane-2-carboxylate (20, R = CH_3, R′ = OC_2H_5) from 5, R = CH_3, and Ethyl Chloroformate. To a 1:1 (v/v) mixture of THF and the chlorformate (0.2 mol) was added with stirring in a −73° bath within 20 min a solution of 10 mmol of the anion in 40 ml of THF–hexane. After 2 hr the mixture had reached −5°. The flask was connected through a large cold trap kept at −78° to remove solvents and most of the excess acid chloride under *ca.* 5 mm. The residue was dissolved in water and ether. From the organic layer a 60% yield of dithiane ester was isolated: bp 95° (0.3 mm); n^{28}D 1.5182; ir (neat) 3.34, 3.40, 5.78, 6.90, 7.80, 8.12, 8.62, 9.04, 9.76, and 11.51 μ; nmr (CCl_4) 8.69 (t, J = 7.2 Hz, ethyl CH_3), 5.83 (q, J = 7.2 Hz, ethyl CH_2), 8.43 (s, CH_3). *Anal.* Calcd for $C_8H_{14}O_2S_2$: C, 46.60; H, 6.84; O, 15.52; S, 31.04. Found: C, 46.67; H, 6.90; O, 15.64; S, 30.92.

(5) 2-Acetyl-2-methyl-1,3-dithiane (20, R = R′ = CH_3) and Bis(1,3-propylenedithioacetal) of 3-Hydroxy-3-methylpentane-2,4-dione (22, R = R′ = CH_3) from 5, R = CH_3, and Acetyl Chloride. Using exactly the procedure described for the reaction with ethyl chloroformate, section b4, a 30-fold excess of acetyl chloride was combined at −78° with the anion solution (17.15 mmol) within 50 min with rapid stirring. Yield of ketone, 1.50 g (50%): bp 72° (0.2 mm); n^{24}D 1.5455; ir (neat) 3.39, 5.86, 6.93, 7.05, 7.54, 8.32, 9.26, 10.45, and 11.50 μ; nmr (CCl_4) 7.74 (s, $COCH_3$), 8.23 (s, CH_3). *Anal.* Calcd for $C_7H_{12}OS_2$: C, 47.72; H, 6.87; O, 9.08; S, 36.33. Found: C, 47.76; H, 6.67; O, 9.24; S, 36.19. 2,4-Dinitrophenylhydrazone: mp 183.5–184.2° (yellow needles, clustered to plates, from ethanol). *Anal.* Calcd for $C_{13}H_{16}N_4O_4S_2$: C, 43.81; H, 4.52; N, 15.72; O, 17.96; S, 17.99; Found: C, 44.37; H, 4.52; N, 15.41; O, 17.95; S, 17.95. Adding the anion solution within 20 min at −20° to excess acetyl chloride and within 15 min at −5° to excess ethyl acetate furnished 30 and 51%, respectively, of the 2:1 alcohol adduct under otherwise identical conditions. The alcohol can be re-

crystallized from methanol: mp 99.5–100.0°; ir ($CHCl_3$) 2.80, 3.29, 3.35, 3.50, 6.93, 7.07, 7.28, 7.83, 8.08, 8.72, and 9.25 μ; nmr ($CDCl_3$) 7.95 (s, 2-dithiane CH_3), 8.21 (s, CH_3), 6.6 (s, OH). *Anal.* Calcd for $C_{12}H_{22}OS_4$: C, 46.45; H, 7.17; O, 5.16; S, 41.25. Found: C, 46.51; H, 6.93; O, 5.31; S, 41.11.

(6) 2-Hexahydrobenzoyl-2-methyl-1,3-dithiane (20, R = CH_3, R′ = C_6H_{11}) from 5, R = CH_3, and Cyclohexane Carboxylic Ester. A solution of 17.0 mmol of the lithium compound was added dropwise within 12 min at −60° to 1.37 g (8.8 mmol) of the ethyl ester in 15 ml of THF. The bath temperature was allowed to warm to −10° within 70 min and the mixture was kept 1 day in a refrigerator. The usual work-up with chloroform and distillation (200° (0.1 mm)) gave 60% of a colorless oil: ir (neat) 3.35, 5.87, 6.92, 7.33, 9.36, and 10.13 μ; nmr (CCl_4) 2.25 (s, 2-dithiane CH_3).

(7) Bis(1,3-propylenedithioacetal) of 3-hydroxy-3-phenylpentane-2,4-dione (22, R = CH_3, R′ = C_6H_5) from 5, R = CH_3, and Ethyl Benzoate. Neat ester (388 mg, 2.58 mmol) was added to a solution of 5.64 mmol of metalated 2-methyl-1,3-dithiane at 0°. After removing the ice bath stirring was continued for 1 hr. Work-up with chloroform–water gave rise to 931 mg (96.6%) of product **22** as colorless crystals, mp 151–155°. The analytical sample was prepared by recrystallization from CH_3OH–$CHCl_3$ 3:1: mp 156.5–158.0°; ir ($CHCl_3$) 2.84, 3.20, 3.28, 3.35, 3.49, 6.70, 6.92, 7.07, 7.28, 7.83, 8.60, 9.31, 9.74, and 14.2 μ; nmr ($CDCl_3$) 7.85 (s, CH_3), 5.58 (s, OH), 2.0 (broad m, C_6H_5), and 2.7 (narrow m, C_6H_5). *Anal.* Calcd for $C_{17}H_{24}OS_4$: C, 54.83; H, 6.50; O, 4.29; S, 34.38. Found: C, 54.72; H, 6.55; O, 4.41; S, 34.12.

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Registry No.—**5** (R = $(C_2H_5O)_2CHCH_2$), 53178-53-3; **6** (R = *t*-C_4H_9), 6007-21-2; **6** (R = cyclohexen-1-yl-4), 53178-49-7; **6** (R = H), 505-23-7; **6** (R = 1-chlorocyclohexyl-1), 53178-50-0; **15**, 53178-54-4; **17**, 53209-81-7; **18** (R′ = C_6H_5, R″ = H), 17590-58-8; **18** (R′ = R″ = C_6H_5), 36998-40-0; **18** (R′ = R″ = $(CH_2)_5$), 37891-71-7; **19**, 5849-28-5; **20** (R = H, R′= OH), 20461-89-6; **20** (R = CH_3, R′ = OH), 4901-19-3; **20** (R = *t*-C_4H_9, R′ = OH), 4882-94-4; **20** (R = H, R′ = OC_2H_5), 20462-00-4; **20** (R = H, R′ = styryl), 4883-02-7; **20** (R = CH_3, R′ = H), 4882-97-7; **20** (R = CH_3, R′ = H) DNPH, 5849-01-4; **20** (R = CH_3, R′ = OEt), 4882-95-5; **20** (R = R′ = CH_3), 5011-99-4; **20** (R = R′ = CH_3) DNPH, 53178-55-5; **20** (R = CH_3, R′ = C_6H_{11}), 4882-98-8; **22** (R = H, R′ = styryl), 4883-03-8; **22** (R = R′ = CH_3), 4882-99-9; **22** (R = CH_3, R′ = C_6H_5), 4883-00-5; propane-1,3-dithiol, 109-80-8; propionaldehyde, 123-38-6; hexanal, 66-25-1; pivalaldehyde, 630-19-3; methyl glyoxal bis(1,3-propylene)dithioacetal, 53178-56-6; cyclohexene-1-carboxyaldehyde-4, 100-50-5; benzalanilide, 93-98-1; ethyl chloroformate, 541-41-3; ethyl cinnamate, 103-36-6; dimethylformamide, 68-12-2; epichlorohydrin, 106-89-8; acetyl chloride, 75-36-5; ethyl cyclohexanecarboxylate, 3289-28-9; ethyl benzoate, 93-89-0.

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Transfer Hydrogenation and Transfer Hydrogenolysis. V. Hydrogen Transfer from Amines, Ethers, Alcohols, and Hydroaromatic Compounds to Olefins Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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In the hydrogen transfer from organic compounds to olefins catalyzed by $RhCl(PPh_3)_3$, some cyclic amines were found much more reactive than oxygenated and hydroaromatic compounds such as primary and secondary alcohols, tetralin, etc. Reactivity decreased in the order indoline > pyrrolidine > tetrahydroquinoline > piperidine > 2,3-butanediol > dioxane > cyclohexanol > isopropyl alcohol. Indoline and tetrahydroquinoline gave stoichiometrically indole and quinoline, respectively.

The transfer of hydrogen to olefins from hydroaromatic compounds and primary and secondary alcohols[2] is heterogeneously catalyzed. Alcohols,[3] arylaldehydes,[4] *N*-methylformamide,[4] formic acid,[4] and dioxane[5] have been reported as hydrogen sources in homogeneous reactions.

This paper reports on investigation of the hydrogen-donating ability of various organic compounds catalyzed by chlorotris(triphenylphosphine)rhodium(I), which has high catalytic activity in the reduction of olefins by molecular hydrogen.[6] It was found that some cyclic amines such as