# Silicon-Containing Carbanions. II. Ketene Thioacetal Synthesis via 2-Lithio-2-trimethylsilyl-1,3-dithiane

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2-Lithio-2-trimethylsilyl-1,3-dithiane (1) reacts with aldehydes and ketones to afford ketene thioacetals (2) directly in good yields. The carbonyl compounds employed included aromatic ketones, hindered, enolizable aldehydes and ketones, and  $\alpha,\beta$ -unsaturated aldehydes and ketones. The latter underwent exclusive 1.2 addition to the carbonyl group. Several of the ketene thioacetals were reduced to thioacetals by a protonation-hydride transfer sequence using trifluoroacetic acid and triethylsilane in methylene chloride to illustrate the usefulness of the reaction as a synthetic method for accomplishing the conversion of R1R2CO to R1R2CHCHO. Evidence is presented to indicate that the stabilization of an adjacent carbonium ion by electron release from sulfur is appreciable.

Organolithium reagents which bear a trimethylsilyl substituent at the carbanionic center react smoothly with aldehydes and ketones according to eq  $1.^{1-3}$  In



most cases, the decomposition of the presumed intermediate is spontaneous and the olefin products are obtained directly and in good yield.

This modification of the Wittig-Horner olefin synthesis holds great promise for organic transformations, particularly in the preparation of heteroatom-substituted olefins. Described here is an extension of this method to the synthesis of ketene thioacetals (2) by the reaction of aldehydes and ketones with 2-lithio-2-trimethylsilyl-1,3-dithiane (1) (eq 2).<sup>3a</sup>

In addition to possessing an interesting  $\pi$  system, ketene thioacetals are proving to be useful synthetic intermediates.<sup>4</sup> Thus, 2 can be converted to a carboxylic acid by hydrolysis, the overall reaction sequence being one which converts R1R2CO to R1R2-CHCO<sub>2</sub>H.<sup>5,6</sup> The conversion of R<sub>1</sub>R<sub>2</sub>CO to R<sub>1</sub>R<sub>2</sub>-CHCHO via 2 can also be accomplished, since reduction of the double bond of 2 leads to the thioacetal 3of R<sub>1</sub>R<sub>2</sub>CHCHO. This reduction is readily carried out by the protonation-hydride transfer sequence shown in eq 3.7

Corey and Seebach have described the metalation of 2-substituted 1,3-dithianes (3) and shown how the resulting organolithium reagents function as nucleophilic carbonyl equivalents.<sup>5,8</sup> Therefore, conversion

(2) F. A. Carey and A. S. Court, J. Org. Chem., 37, 939 (1972).

(3) T. H. Chan, E. Chang, and E. Vinokur, Tetrahedron Lett., 1137 (1970). (3a) NOTE ADDED IN PROOF.—Professor Dieter Seebach (Giessen) has independently developed a similar ketene thioacetal synthesis based on 1 which will be described in a forthcoming publication.

(4) R. M. Carlson and P. M. Helquist, *ibid.*, 173 (1969).
(5) D. Seebach, *Synthesis*, 17 (1969).

(6) J. A. Marshall and J. L. Belletire, Tetrahedron Lett., 871 (1971).

(7) F. A. Carey and J. R. Neergaard, J. Org. Chem., 36, 2731 (1971).

(8) E. J. Corey and D. Seebach, Angew. Chem., Int. Ed. Engl., 4, 1075 (1965).



of R<sub>1</sub>R<sub>2</sub>CO to R<sub>1</sub>R<sub>2</sub>CHCOR<sub>8</sub> by reaction of the anion of 3 with alkyl halides followed by hydrolysis<sup>9</sup> is a practical process.

Existing methods for the synthesis of ketene thioacetals suffer from a lack of generality. Most procedures involve alkylation of the intermediates resulting from reaction of carbanions with carbon disulfide and are limited to substrates such as diethyl malonate and nitromethane which form stable carbanions. Corev and Märkl<sup>10</sup> have developed a highly selective ketene thioacetal synthesis employing ylide 4 which reacts with aldehydes but not ketones.

$$(MeO)_{3}P \xrightarrow{S} + RCHO \rightarrow \underset{H}{\overset{R}{\longrightarrow}} \xrightarrow{S} + (MeO)_{3}PO$$

A novel fragmentation leading to ketene thioacetals has been reported by Marshall,<sup>6</sup> e.g.

(9) (a) E. J. Corey and B. W. Erickson, J. Org. Chem., 36, 3553 (1971);
(b) E. Vedejs and P. L. Fuchs, *ibid.*, 36, 366 (1971).

(10) E. J. Corey and G. Märkl, Tetrahedron Lett., 3201 (1967).

<sup>(1)</sup> D. J. Peterson, J. Org. Chem., 33, 780 (1968).

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Addition of the anion of 1,3-dithiane to aldehydes and ketones yields alcohols which can be converted to ketene thioacetals by subsequent acid-catalyzed dehydration or by dehydrohalogenation of the derived chloride.<sup>5,8</sup>

#### **Results and Discussion**

Synthesis of Ketene Thioacetals.—Metalation of 2trimethylsilyl-1,3-dithiane by *n*-butyllithium in tetrahydrofuran to afford 1 has been described by Corey<sup>11</sup> and by Brook<sup>12</sup> who used this reagent for the synthesis of  $\alpha$ -silyl ketones. Reaction of 1 with aldehydes and ketones is rapid and efficient and produces ketene thioacetals 2 as the first isolable product. The results of a number of reactions summarized in Table I and eq 2

TABLE I

REACTION	S OF	1	WITH	ALDEHYDES	AND	Ketones	
<i>~</i> , ,				T.			

Carbonyl compd	Product	Yield, % <sup>a</sup>
Benzophenone	2a	78
Dicyclopropyl ketone	2b	68
Tiglaldehyde	2c	80
Cinnamaldehyde	2d	70
Isobutyraldehyde	2e	44
Cyclohexanone	2f	62
Cyclohexenone	2g	40
Adamantanone	2h	95
2-Norbornanone	2i	64
1,2-O-Isopropylidene-D-		
glycero-tetros-3-ulose	2j	25

<sup>a</sup> The yields are based on isolated amount of purified product and are not corrected for recovered starting material.

serve to indicate the varied types of ketene thioacetals which can be prepared by this method. The carbonyl compounds employed include aromatic and aliphatic ketones, enolizable aldehydes and ketones,  $\alpha,\beta$ -unsaturated aldehydes and ketones, and sterically hindered ketones. Evidence in support of the ketene thioacetal structures was obtained by conventional analytical and spectroscopic means and is presented in the Experimental Section along with pertinent physical constants. Reagent 1 reacts well with unhindered or nonenolizable ketones but is less effective toward addition to hindered, enolizable substrates such as isobutyraldehyde. No ketene thioacetal was obtained when 1 was allowed to react with pinacolone. The keto sugar 1,2-O-isopropylidene-D-glycero-tetros-3-ulose  $(5)^{13}$  also gave low yields of 2j.

Only 1,2 addition was observed with  $\alpha,\beta$ -unsaturated aldehydes and ketones to produce the unsaturate ketene thioacetals.

Reaction of 1 with tetraphenylcyclopentadienone did not lead to the formation of the expected carbonyl

(11) E. J. Corey, D. Seebach, and R. Freedman, J. Amer. Chem. Soc., 89, 434 (1967).

(12) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *ibid.*, **89**, 431 (1967).



addition product 8 but instead gave the products of electron transfer, tetraphenylcyclopentenone (6) and the dimer  $7.^{14}$ 



Conversion of Ketene Thioacetals to 3.—Several of the ketene thioacetals prepared by the above procedure were converted to the corresponding aldehydes to illustrate the use of these intermediates in synthetic problems. Benzophenone was converted to diphenylacetaldehyde by way of reduction of 2a to 3 ( $R_1 = R_2 = Ph$ ) followed by oxidative hydrolysis of 3 to  $Ph_2CHCHO$ . The reduction step was accomplished in 87% yield with triethylsilane and trifluoroacetic acid in methylene chloride (eq 3) and the hydrolysis step in 70% yield using N-bromosuccinimide in acetonitrile-water.<sup>9a</sup>

In similar fashion 2f was prepared from cyclohexanone and reduced to 2-cyclohexyl-1,3-dithiane [3,  $R_1 + R_2 = -(CH_2)-_5$ ] in 63% yield, which was then hydrolyzed to cyclohexanecarboxyaldehyde in 93% yield.

The diphenyl and dicyclopropyl ketene thioacetals (2a and 2b) proved very useful in determining the site of protonation of the double bond in ketene thioacetals. Evidence was provided previously that the site of protonation of the ferrocene-derived ketene thioacetal 2k is the carbon atom adjacent to the ferrocene to give the sulfur-stabilized carbonium ion 9 rather than at the dithiane ring position to give the ferrocenylmethyl cation 10. This implies a high de-



gree of stabilization by sulfur, presumably by electron donation using the lone pairs, of an adjacent carbonium ion since it is well established that ferrocenylmethyl cations are very stable ions.<sup>15</sup> We have examined this

(14) Oxidative dimerization of anions of 1,3-dithiane has been observed; see ref 5 and 8.

(15) E. A. Hill and R. Wiesner, J. Amer. Chem. Soc., 91, 509 (1969); J. Feinberg and M. Rosenblum, *ibid.*, 91, 4324 (1969).

 <sup>(13)</sup> F. A. Carey, D. H. Ball, and L. Long, Jr., Carbohyd. Res., 3, 205
 (1966); D. H. Ball, F. A. Carey, I. L. Klundt, and L. Long, Jr., *ibid.*, 10, 121 (1969).

question in more detail and confirm our original conclusions regarding the stabilization by sulfur.

Ketene thioacetal 2b was prepared and the site of protonation was studied by nmr. Regioselective protonation of the double bond was observed to produce the sulfur-stabilized carbonium ion 9b in preference to the cyclopropyl-stabilized ion 10b.<sup>16</sup> Addition of trifluoroacetic acid to a solution of 2b in deuteriochloroform in an nmr tube led to the appearance of a new species characterized by a one-proton triplet of  $\delta_{\text{TMS}}$  2.8 assigned to the methine proton in ion 9. The signals assigned to the  $-SCH_2$  protons in 2b undergo a downfield shift of 0.7 ppm on protonation consistent with development of positive charge in the dithiane ring. Moreover, in contrast to the behavior observed with cyclopropylmethyl cations generated under similar conditions, the cyclopropyl rings remain intact as shown by the signals at  $\delta$  0.2-0.8 and 1-1.3. From previous observations with cyclopropylmethyl cations, we would expect that, if protonation had occurred to give a cyclopropyl-stabilized carbonium ion. ring-opening to yield a 3-butenyl trifluoroacetate would have been rapid.<sup>17</sup>

The diphenyl ketene thioacetal 2a was also shown to produce a sulfur-stabilized carbonium ion (9a) on protonation by a labeling experiment in which 2awas converted to 11 with trifluoroacetic acid-d and triethylsilane. Under these conditions the monodeuterated thioacetal was obtained, as evidenced by nmr and mass spectrometry.

Undeuterated 11 exhibits an AB quartet (J = 10)Hz) in which the center of gravity of the doublet at lower field is 4.79 ppm from internal TMS and the doublet at higher field is at 4.15 ppm. The spectrum of deuterated material has a single peak at 4.79 ppm corresponding to addition of a single deuterium to the double bond. The mass spectrum was also in accord with monodeuteration, as evidenced by the fragment at m/e 287 for the molecular ion. The position of deuteration was determined from the mass spectrum to be at the carbon atom bearing the two phenyls. The base peak in the spectrum of 11 is at m/e 119 and corresponds to fragment ion 12. Since this is also the base peak in deuterated product it follows that Scheme I correctly describes the reaction path.

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These observations that carbonium ions at the 2 position of a 1,3-dithiane are formed preferentially to diphenylmethyl cations, dicyclopropylmethyl cations, and ferrocenylmethyl cations lead to the con-

(16) For an exhaustive list of references on cyclopropylmethyl cations see P. v. R. Schleyer and V. Buss, J. Amer. Chem. Soc., **91**, 5880 (1969).

clusion that stabilization by electron release from sulfur is appreciable and that sulfur is at least as stabilizing a substituent as cyclopropyl.<sup>18</sup>

#### **Experimental Section**

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in  $CDCl_3$  and chemical shifts are reported in parts per million ( $\delta$ ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr disks for solids and pressed films for liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV.

Microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany.

All reactions involving organolithium reagents were carried out in an atmosphere of dry nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride. *n*-Butyllithium in hexane was purchased from Alfa Inorganics.

General Procedure for Synthesis of Ketene Thioacetals.—To a solution of 1.92 g (10 mmol) of 2-trimethylsilyl-1,3-dithiane in 10 ml of dry tetrahydrofuran was added 4.5 ml (10 mmol) of a solution of *n*-butyllithium in *n*-hexane. After stirring for 15 min at 0° a solution of 10 mmol of the aldehyde or ketone in 5 ml of tetrahydrofuran was added and the reaction mixture was maintained at 0° for 15 min, then 15 min at 25°. Brine (15 ml) was added and the product was extracted with two 10-ml portions of ether, dried (MgSO<sub>4</sub>), filtered, and evaporated to yield the crude product.

2-Diphenylmethylene-1,3-dithiane (2a).—Recrystallization of the crude product from reaction of benzophenone with 1 from ethanol gave 2.20 g (78%) of 2a, mp 133.5-135.5° (reported<sup>5,8</sup> mp 134.5-135°).

2-(1,1-Dicyclopropyl)methylene-1,3-dithiane (2b).—Evaporative distillation of the crude product from reaction of dicyclopropyl ketone with 1 at  $125^{\circ}$  (0.1 mm) afforded 1.44 g (68%) of 2b as a clear liquid: nmr (CDCl<sub>3</sub>)  $\delta$  0.6–0.8 (m, 8, cyclopropyl CH<sub>2</sub>), 1.2–1.6 (m, 2, cyclopropyl CH), 2.1 (q, 2, CCH<sub>2</sub>C), 2.9 (t, 4, -SCH<sub>2</sub>).

The analytical sample was obtained by preparative tlc on silica gel using cyclohexane as the solvent.

Anal. Calcd for  $C_{11}H_{16}S_2$ : C, 62.20; H, 7.59. Found: C, 62.10; H, 7.42.

2-(2-Methyl-2-butenylidene)-1,3-dithiane (2c).—Tiglaldehyde (25 mmol) in 10 ml of tetrahydrofuran was added to a solution of 25 mmol of 1 in 10 ml of tetrahydrofuran and worked up as described above to afford 4.3 g of crude product. Distillation afforded 3.7 g (80%) of 2c: bp 97-98° (0.35 mm); nmr (CDCl<sub>3</sub>)  $\delta$  1.7 (d, 3, J = 7 Hz, CH<sub>3</sub>CH=), 1.82 (s, 3, CH<sub>3</sub>C=), 2-2.3 (m, 2, SCHCH<sub>2</sub>), 2.7-3 (m, 4, SCH<sub>2</sub>), 5.5 (q, 1, J = 7 Hz, CH<sub>3</sub>-CH=), 6.3 (s, 1, HC=C). Distillation apparently resulted in cis-trans isomerization of the double bond '(acid-catalyzed?), since the purified product showed an additional vinyl H singlet at  $\delta$  6.42 and an additional CH<sub>3</sub>CH= quartet centered at  $\delta$  5.3. Anal. Calcd for CH-S: C 58 01: H 757 Found: C

Anal. Caled for C<sub>9</sub>H<sub>14</sub>S<sub>2</sub>: C, 58.01; H, 7.57. Found: C, 57.90; H, 7.41.

2(3-Phenyl-2-propenylidene)-1,3-dithiane (2d).—From 25 mmol of 1 and 25 mmol of *trans*-cinnamaldehyde in tetrahydro-furan was obtained 6.28 g of crude product which deposited 4.0 g of 2d as yellow crystals from hexane-ether, mp 84° (reported<sup>10</sup> mp 86-87°). The nmr spectrum was identical with that of authentic material prepared as described in ref 10: nmr (CDCl<sub>3</sub>)  $\delta$  2.0-2.4 (m, 2, SCH<sub>2</sub>CH<sub>2</sub>), 2.8-3.1 (m, 4, SCH<sub>2</sub>), 6.58 (d, 1, J = 15 Hz), 6.63 (d, 1, J = 10 Hz), 7-7.6 (m, 6, aromatic + vinyl).

2(2-Methylpropylidene)-1,3-dithiane (2e).—Distillation of the crude product from 25 mmol of isobutyraldehyde and 1 gave 3.4 g of material, bp 84-89° (1.5 mm), contaminated with 2trimethylsilyl-1,3-dithiane. A 400-mg portion was purified by preparative tlc to give 223 mg of 2e as a colorless liquid corresponding to a net yield of 44%.

2-Cyclohexylidene-1,3-dithiane (2f).—The condensation of cyclohexanone with 1 was performed on a 25-mmol scale and the

<sup>(17)</sup> F. A. Carey and H. S. Tremper, ibid., 91, 2969 (1969).

<sup>(18)</sup> G. A. Russell and L. A. Ochrymowycz, J. Org. Chem., **35**, 764 (1969), have suggested on the basis of hydrolysis experiments that the ion Ph<sub>2</sub>CCH  $(SCH_3)_2^+$  is more stable than Ph<sub>2</sub>CHC $(SCH_3)_2^+$ . The reaction on which this comparison was based is a complicated one which may involve episulfonium ion intermediates and, therefore, is subject to some uncertainty.

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crude product was recrystallized from ethanol to yield 3.09 g (62%) of 2f, mp 91.5-93.5° (reported<sup>5</sup> mp 93.6-94°).

**3**-[2-(1,3-dithianylidene)] cyclohexene (2g).—Cyclohexenone (25 mmol) on reaction with 25 mmol of 1 afforded, after recrystallization of the crude product from ethanol, 2.0 g of 2i as white crystals: mp 59°; nmr (CDCl<sub>3</sub>)  $\delta$  1.7 (q, 2, CH<sub>2</sub> at C-5 of cyclohexenyl), 2-2.3 (m, 4, CH<sub>2</sub> at C-6 of cyclohexenyl and SCH<sub>2</sub>CH<sub>2</sub>), 2.5 (t, 2, CH<sub>2</sub> at C-4 of cyclohexenyl), 2.9 (m, 4, SCH<sub>2</sub>), 5.8 (d of t, 1, H at C-1 of cyclohexenyl,  $J_{1.2} = 10, J_{1.5} =$ 3 Hz), 6.7 (d of t, 1, H at C-2 of cyclohexenyl,  $J_{2.6} \cong 1$  Hz).

Anal. Calcd for C<sub>10</sub>H<sub>14</sub>S<sub>2</sub>: C, 60.55; H, 7.11. Found: C, 60.29; H, 7.11.

2[2-(1,3-dithianylidene)]adamantane (2h).—Adamantanone (10 mmol) and 1 reacted to afford a clear sirup which was chromatographed on 60 g of Woelm silica gel and eluted with methylene chloride to yield 2.41 g (95%) of 2h as a sirup which deposited 1.44 g (57%) of pure product on crystallization from ethanol: mp 45-46°; nmr (CDCl<sub>3</sub>)  $\delta$  1.5-2.3 (broad envelope, 14, CH<sub>2</sub> and CH), 2.8 (m, 4, -SCH<sub>2</sub>), 3.3 (broad s, 2, allylic CH). Anal. Calcd for Cl<sub>4</sub>H<sub>20</sub>S<sub>2</sub>: C, 66.62; H, 7.98. Found: C, 66.50; H, 7.74.

2-[2-(1,3-dithianylidene)]norbornane (2i).—Reaction of 1 with 2-norbornanone was done on a 25-mmol scale. The crude product was stripped of volatile impurities at 0.1 mm to leave 3.2 g (64%) of product which crystallized on cooling: nmr (CDCl<sub>3</sub>)  $\delta$  1-1.8 (m, 6, CH<sub>2</sub> at C-5, -6, and -7 of norbornyl), 2-2.6 (m, 5, CH<sub>2</sub> at C-5 of dithiane plus CH<sub>2</sub> at C-3 and C-H at C-4 of norbornyl), 2.5-3 (m, 4, -SCH<sub>2</sub>), 3.3 (broad s, 1, CH at C-1 of norbornyl).

The analytical sample was obtained by recrystallization from ethanol, mp  $37-38^{\circ}$ .

Anal. Ĉaled for  $C_{11}H_{16}S_2$ : C, 62.20; H, 7.59. Found: C, 62.09; H, 7.42.

1,2-O-Isopropylidene-3-[2-(1,3-dithianylidene]-D-glycero-tetrose (2j).—From 3.8 mmol of 1,2-O-isopropylidene-D-glycero-tetros-3ulose and 4 mmol of 1 was obtained 1.06 g of crude product which was stripped of volatile impurities at 0.1 mm. Preparative tlc on silica gel gave 230 mg (24%) of 2j as a clear sirup which crystallized on standing: nmr (CDCl<sub>3</sub>)  $\delta$  1.39 and 1.45 (two s, 6, isopropylidene CH<sub>3</sub>), 2-2.4 (m, 2, SCHCH<sub>2</sub>), 2.8-3 (m, 4, SCH<sub>2</sub>), 4.53 (s, 2, CH<sub>2</sub> at C-4), 5.16 (d, 1,  $J_{1,2} = 4$  Hz, CH at C-2),  $\delta$ .82 (d, 1,  $J_{1,2} = 4$  Hz, anomeric CH).

The analytical sample was obtained by recrystallization from cyclohexane, mp 75°.

Anal. Calcd for  $C_{11}H_{16}O_{3}S_{2}$ : C, 50.74; H, 6.19; S, 24.63. Found: C, 50.54; H, 6.33; S, 24.75.

**Reaction of 1 with Tetraphenylcyclopentadienone.**—This reaction was carried out on a 5.2-mmol scale and the crude product (3.1 g) was purified by preparative tle on silica gel using cyclohexane as the solvent. From 310 mg of crude product was eluted first 50 mg (50%) of 2-trimethylsilyl-2-(2-trimethylsilyl-1,3-dithianyl)-1,3-dithiane (7): mp 122°; nmr (CDCl<sub>3</sub>)  $\delta$  0.38 (s, 18, SiMe<sub>3</sub>), 1.8-2.5 (m, 4, -SCH<sub>2</sub>CH<sub>2</sub>), 3.4-3.8 (m, 8, -SCH<sub>2</sub>); mass spectrum (70 eV) m/e (rel intensity) 382 (2), 193 (26), 192 (29), 191 (100), 149 (20), 73 (55).

Anal. Calcd for  $C_{14}H_{50}S_1S_{12}$ : C, 43.92; H, 7.90; S, 33.51. Found: C, 44.07; H, 7.68; S, 33.41.

The second product eluted was tetraphenylcyclopentadienone (50 mg, 25%), mp 160–162° (reported<sup>19</sup> mp 162–163°). The most polar product, a yellow oil identified as 1-*n*-butyl-2,3,4,5-tetraphenylcyclopentadienol<sup>20</sup> from its ir, nmr, and mass spectrum, was isolated in 45% yield.

**Reduction of 2a by Hydride Transfer.**—To a solution containing 284 mg (1 mmol) of **2a** and 0.2 ml of triethylsilane in 5.0 ml of methylene chloride was added 0.5 ml of trifluoroacetic acid. The resulting red solution was allowed to stand for 24 hr. Saturated sodium bicarbonate solution was added and the layers were separated. The aqueous phase was extracted with 10 ml

(20) A. G. Bonagura, M. B. Meyers, S. J. Storfer, and E. I. Becker, *ibid.*, **76**, 6122 (1954).

of methylene chloride and the combined organic extracts were dried over magnesium sulfate and evaporated. Recrystallization of the resulting product from ethanol gave 250 mg (87%) of 2-diphenylmethyl-1,3-dithiane as white crystals, mp 115–117°, which were identical with authentic material.

Authentic material was prepared by reaction of diphenylacetaldehyde with 1,3-propanedithiol in boron trifluoride etherate. The analytical sample was obtained as white needles by recrystallization from ethanol: mp 119-120°; nmr (CDCl<sub>3</sub>)  $\delta$  1.9-2.2 (m, 2, SCH<sub>2</sub>CH<sub>2</sub>), 2.7-2.9 (m, 4, SCH<sub>2</sub>), 4.15 (d, 1, J = 10 Hz, HCPh<sub>2</sub>), 4.79 (d, 1, J = 10 Hz, HCS<sub>2</sub>), 7.3 (s, 10, aromatic); mass spectrum (70 eV) m/e (rel intensity) 286 (4), 167 (10), 166 (6), 165 (18), 121 (11), 120 (6), 119 (100).

aromatic), mass spectrum (10 ev) m/e (rel intensity) 286 (4), 167 (10), 166 (6), 165 (18), 121 (11), 120 (6), 119 (100). Anal. Calcd for  $C_{17}H_{18}S_2$ : C, 71.28; H, 6.34; S, 22.38. Found: C, 70.92; H, 6.27; S, 22.58.

Reduction of 2a with Triethylsilane-CF<sub>3</sub>CO<sub>2</sub>D.—A solution of trifluoroacetic acid-d in 10 ml of methylene chloride was prepared from 1 ml (1.49 g, 7 mmol) of trifluoroacetic anhydride and 0.14 ml (154 mg, 7.7 mmol) of D<sub>2</sub>O. A 5-ml portion of this solution was added to 284 mg (1 mmol) of 2a and 0.2 ml of triethylsilane and the reaction mixture was worked up as in the preceding experiment to afford 205 mg (72%) of deuterated 11, mp 117-120°. The nmr spectrum was identical with that of authentic material except for the disappearance of the doublet at  $\delta$  4.15 and the collapse of the doublet at  $\delta$  4.79 to a broadened singlet; mass spectrum (70 eV) m/e (rel intensity) 287 (3), 284 (6), 168 (6), 167 (3), 166 (9), 165 (5), 121 (12), 120 (7), 119 (100).

Hydrolysis of 2-Diphenylmethyl-1,3-dithiane.—A solution containing 2.0 g (7 mmol) of the 2-substituted dithiane in 12 ml of acetonitrile was added to a solution of 7.4 g (42.0 mmol) of N-bromosuccinimide in 60 ml of 4:1 acetonitrile-water and stirred for 5 min at 0°. The solution was added to 200 ml of saturated sodium sulfite solution and extracted with 400 ml of 1:1 hexane-methylene chloride. The organic phase was washed with 200 ml of 1 M sodium bicarbonate, 200 ml of water, and 200 ml of brine and dried over magnesium sulfate. Evaporation of the solvent at 25° gave 950 mg (70%) of pure product, the ir spectrum of which was identical with that of authentic diphenylacetaldehyde;<sup>21a</sup> nmr (CDCl<sub>3</sub>)  $\delta$  4.79 (d, 1, J = 2 Hz, Ph<sub>2</sub>CH), 7.2 (s, 10, aromatic), 9.80 (d, 1, J = 2 Hz, aldehyde CH).

Conversion of 2f to Cyclohexanecarboxaldehyde.—A solution containing 400 mg (2.0 mmol) of 2f, 1.0 ml of trifluoroacetic acid, and 0.4 ml of triethylsilane in 10 ml of methylene chloride was allowed to stand for 20 hr and then poured into 30 ml of saturated sodium bicarbonate. The layers were separated, the aqueous phase was extracted with a further 10-ml portion of methylene chloride, and the combined organic extracts were dried over magnesium sulfate. Evaporation of the methylene chloride left a sirup which crystallized. Recrystallization from ethanolwater afforded 254 mg (63%) of 2-cyclohexyl-1,3-dithiane, mp  $51.5-52.5^{\circ}$  (reported<sup>5</sup> mp 51.6-52.4°).

Hydrolysis of 450 mg (2.22 mmol) of this material was accomplished by adding a solution of it in 3.0 ml of acetonitrile to 2.37 g (13.3 mmol) of N-bromosuccinimide in 15 ml of 4:1 acetonitrile-water and stirring for 5 min. The work-up was on one-fourth the scale of the preceding experiment and yielded 243 mg (93%) of cyclohexanecarboxaldehyde which was identical in respect to ir spectrum with that reported.<sup>21b</sup>

**Registry No.**—1, 34410-04-3; 2b, 34399-58-1; 2c, 34399-59-2; 2g, 34399-60-5; 2h, 34399-61-6; 2i, 34399-62-7; 2j, 34399-63-8; 7, 34399-64-9; 11, 34399-65-0; 2-diphenylmethyl-1,3-dithiane, 34399-66-1; diphenylacetaldehyde, 947-91-1.

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(21) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., 1970: (a) Spectrum 674C; (b) Spectrum 217E.

 <sup>(19) (</sup>a) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, J. Amer. Chem. Soc., 75, 2283 (1953);
 (b) J. A. Ciabattoni and G. A. Berchtold, J. Org. Chem., 31, 1336 (1966).