Methyl 3-Chloro-2,4,6-trimethylbenzoate (8-Cl).—To a solution of chloromesitylene (31.0 g, 0.20 mol) in 100 ml of chloroform was added, at room temperature, a solution of bromine (35 g, 0.22 mol) in 50 ml of chloroform, in an apparatus equipped with an HBr trap. After being stirred for 3.5 hr, the mixture was washed ($NaHSO_3$, H_2O) and dried ($MgSO_4$). Distillation afforded 33.1 g (0.14 mol, 71%) of **2-bromo-4-chloro-1,3,5-trimethylbenzene**, bp 128–129° (10.5 Torr). The distillate solidified and, after recrystallization from pentane, yielded crystals: mp 57.5–58°; nmr τ 3.13 (s, 1, arom), 7.50, 7.72, 7.86 (s, 3 each, arom CH_3's).

Anal. Calcd for $C_9H_{10}BrCl$: C, 45.89; H, 4.29. Found: C, 46.38; H, 4.51.

A solution of the bromochloride (30 g, 0.129 mol) in 150 ml of dry ether was added dropwise to a suspension of magnesium (3.15 g, 0.129 g-atom) in 150 ml of ether. Reaction was initiated with ethylmagnesium iodide. After Grignard formation was complete, the mixture was poured over crushed Dry Ice. The usual work-up afforded, after two recrystallizations from aqueous acetone, 16.8 g (0.085 mol, 66%) of 3-chloro-2,4,6-trimethylbenzoic acid, mp 145–146° (lit.[29] value 143.5–144.0°).

The acid (5 g, 0.025 mol) in ether was treated with diazomethane. Work-up gave 5.15 g (0.024 mol, 96%) of crude **methyl 3-chloro-2,4,6-trimethylbenzoate (8-Cl)**. Two recrystallizations from petroleum ether (30–60°) gave pure ester: mp 34–34.5°; ir 1725 cm^{-1}; nmr τ 3.19 (s, 1, arom), 6.20 (s, 3, OCH_3), 7.73 (br s, 6, arom CH_3's), 7.83 (s, 3, arom CH_3).

Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.17. Found: C, 62.10; H, 6.11.

Trichloromethylation of Bromomesitylene (7-Br) and Subsequent Methanolysis.—Bromomesitylene (2.01 g, 0.010 mol) in 50 ml of CCl_4, aluminum chloride (2.70 g, 0.020 mol) in 50 ml of CCl_4, 500 ml of ice water, 100 ml of methanol, 20% SE-30 column. In addition to some recovered starting material (ret. time 6.4 min, 8%), two products were obtained, methyl 3-bromo-2,4,6-trimethylbenzoate (24.8 min, 93%) and 4-bromo-2,3,5-trimethylbenzoate (27.8 min, 7%). The former was identical (ir, nmr, retention time) with an authentic sample prepared as described below.

Methyl 3-Bromo-2,4,6-trimethylbenzoate (8-Br).—An ether solution of 3-bromo-2,4,6-trimethylbenzoic acid[29] was treated with diazomethane. The usual work-up afforded a 96% yield of **methyl 3-bromo-2,4,6-trimethylbenzoate**: mp (30–60° petroleum ether) 42.5–43°; ir 1713 cm^{-1}; nmr τ 3.21 (s, 1, arom), 6.22 (s, 3, OCH_3), 7.70 (br s, 6, arom CH_3's), 7.86 (s, 3, arom CH_3).

Anal. Calcd for $C_{11}H_{13}BrO_2$: C, 51.36; H, 5.06. Found: C, 51.49; H, 5.21.

Relative Trichloromethylation Rates.—A suspension of aluminum chloride (2.68 g, 0.020 mol) in 75 ml of carbon tetrachloride was allowed to thermally equilibrate at 40.0 ± 0.1°. A mixture of 0.005 mol each of isodurene and 1 mol of the halomesitylenes in 75 ml of carbon tetrachloride was similarly brought to temperature; the solutions were quickly mixed, stirred for 5 min, and quenched by adding 100 ml of ice water. Solvent was evaporated from the organic layer and the residue was refluxed (2 hr) with 100 ml of aqueous acetone (1:1). The mixture was made strongly alkaline, and unreacted aromatics were extracted with ether and analyzed by vpc.

Registry No.—**8-Br**, 26584-20-3; **8-Cl**, 26584-21-4; **8-F**, 26584-22-5; **8-F** (acid), 26584-23-6; **9-F**, 26584-24-7; **9-F** (acid), 26584-25-8; **11**, 26584-26-9; **12**, 26584-27-0; **12** (acid), 26583-81-3; **13**, 26630-72-8; 3-fluoro-2,4-dimethylbenzy alcohol, 26583-82-4; 3-fluoro-2,4-dimethylbenzyl chloride, 26583-83-5; 6-bromo-3-fluoro-1,2,4-trimethylbenzene, 26583-84-6; 2-bromo-4-chloro-1,3,5-trimethylbenzene, 26583-85-7.

(29) F. M. Beringer and S. Sands, *J. Amer. Chem. Soc.*, **75**, 3319 (1953).

Reduction with Metal-Ammonia Combinations. III.[1] Synthesis of β- and γ-Alkylthiomercaptans from 1,3-Dithiolanes and 1,3-Dithianes

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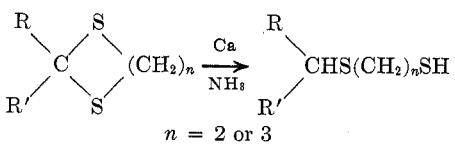
Eleven 1,3-dithiolanes and four 1,3-dithianes have been reduced with calcium in liquid ammonia to give β- and γ-alkylthiomercaptans, $RS(CH_2)_nSH$ (n = 2 or 3), respectively, in high yields.

Part A

Recently, the calcium–ammonia reduction of 1,3-oxathiolanes and 1,3-oxathianes has been reported[1] as a fairly general preparative method for β- and γ-alkoxy mercaptans, respectively. It is evident that selective cleavage of the C–S bond of 1,3-dithiolanes and 1,3-dithianes (Scheme I) would provide a convenient route

SCHEME I



n = 2 or 3

to β-alkylthioethyl and γ-alkylthiopropyl mercaptans. *A priori*, it was not evident whether cleavage of only one of the four C–S bonds in the starting materials shown in Scheme I could be achieved and at the inception of this work there was only one report[2] of such a selective reduction (of 2,2-dimethyl-4-hydroxymethyl-1,3-dithiolane), whereas there were several known instances where reduction led to complete desulfurization[3] or to more complicated products.[4] While this work was in progress,[5] Owen and coworkers[6] published additional examples involving selective cleavage of 2,2-dimethyl-1,3-dithiolanes (Scheme I, R = R′ = CH_3) whereas total cleavage (Scheme II) occurred with 2-methyl- and 2-phenyl-1,3-dithiolanes (R = R′ = H or R = C_6H_5; R′ = H).

As the data in Table I show, reduction according to

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(1) Paper II [E. L. Eliel and T. W. Doyle, *J. Org. Chem.*, **35**, 2716 (1970)] contains an extensive survey of the background literature.

(2) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2938 (1950).

(3) (a) L. A. Stocken, *ibid.*, 592 (1947); (b) R. E. Ireland, T. I. Wrigley, and W. G. Young, *J. Amer. Chem. Soc.*, **80**, 4604 (1958); (c) N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960); (d) R. D. Stolow and M. M. Bonaventura, *Tetrahedron Lett.*, 95 (1964). These reports refer either to benzylic (a) or allylic (b) thioacetals or -ketals or involve reduction with lithium in ethylamine (c, d).

(4) Q. F. Soper, W. E. Buting, J. E. Cochran, and A. Pohland, *J. Amer. Chem. Soc.*, **76**, 4109 (1954); A. Schönberg, E. Petersen, and H. Kaltschmitt, *Ber.*, **66B**, 233 (1933); the latter report involves sodium in ether.

(5) Preliminary report: E. L. Eliel, T. W. Doyle, R. A. Daignault, and B. C. Newman, *J. Amer. Chem. Soc.*, **88**, 1828 (1966).

(6) E. D. Brown, S. M. Iqbal, and L. N. Owen, *J. Chem. Soc. C*, 415 (1966).

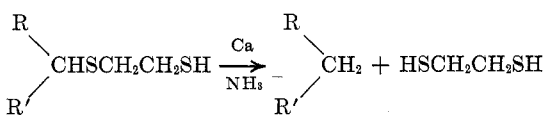
TABLE I

REDUCTION OF 1,3-DITHIOLANES AND 1,3-DITHIANES WITH CALCIUM IN AMMONIA

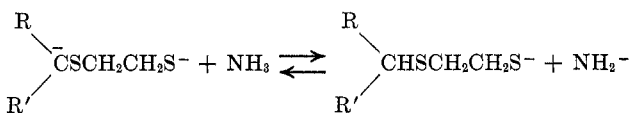
Method[a]	Starting material, ethylene dithioacetal or dithioketal of	Product, R in $RSCH_2CH_2SH$	Yield, %[b] Anal	Yield, %[b] Isold
B	Formaldehyde	Methyl	...[c]	85
A	Acetaldehyde	Ethyl[d]	93, 90	81
A	Propionaldehyde	*n*-Propyl	99, 100	91
A	Isobutyraldehyde	Isobutyl	95, 96	85
A	3-Pentanone	3-Pentyl	97, 98	90
A	Pinacolone	3,3-Dimethyl-2-butyl	98, 99	97
A	*n*-Heptaldehyde	*n*-Heptyl	90 (93), 51 (94)[e]	82
A	Cyclohexanone	Cyclohexyl	92, 93	85
B	Phenylacetaldehyde	2-Phenylethyl	...[c]	94
B	Phenylacetone	1-Phenyl-2-propyl	...[c]	91
A	Hydrocinnamaldehyde	3-Phenyl-1-propyl	98, 99	94
A	Formaldehyde	H	90	60
A	Phenylacetaldehyde	H	97	71
		and ethylbenzene		71
A	Phenylacetone	H	92	76
		and *n*-propylbenzene		79
A	Phenylpentadeuteriopropanone	H	...[c]	...[f]
		and 1-phenyl-1,1,3,3,3-pentadeuteriopropane		65
B	Benzaldehyde	H	...[c]	16
		and toluene		18
	Trimethylene dithioacetal or dithioketal of	R in $RSCH_2CH_2CH_2SH$	Anal	Isold
B	Formaldehyde	Methyl	...[c]	86
A	Isobutyraldehyde	Isobutyl	95, 98	85
A	Cyclohexanone	Cyclohexyl	90, 93	84
A	Formaldehyde	H	97, 98	90
A	α-Hydroxypropionaldehyde	$CH_3CHOHCH_2$–	...[c]	83

[a] Method A, normal addition of an ethereal solution of the 1,3-dithiolane or 1,3-dithiane to an excess of calcium in ammonia. Method B, inverse addition of a limited amount of calcium to an ethereal solution of the 1,3-dithiolane or 1,3-dithiane in ammonia. [b] First column gives analytical yield determined by iodine titration. Second column gives yield of compound isolated. [c] No attempt made to analyze compound. [d] Contaminated with a small amount of an unidentified compound, apparently a mercaptan, not 1,2-ethanedithiol, from thin layer chromatography. [e] The mercaptan is very susceptible to disulfide formation; figures in parentheses refer to the % yields obtained after reduction of disulfide with zinc amalgam (see Experimental Section). [f] No attempt made to isolate compound.

SCHEME II



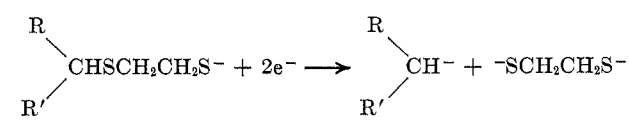
SCHEME III



Scheme I was achieved in the present investigation in almost all cases in nearly quantitative analytical yield; the yields of isolated products ranged from 69 to 97%. In only four cases was overreduction (Scheme II) observed, and in three of these (R = R′ = H and R = $C_6H_5CH_2$; R′ = H or CH_3) it could be effectively prevented by limiting the amount of calcium to the theoretical 2 equiv per mole of thioacetal or thioketal and adding the metal rapidly. Apparently the second reduction stage (Scheme II) is sufficiently slower than the first (Scheme I) in these instances to enable one to achieve high selectivity. Only in the case of benzaldehyde ethylene dithioketal (R = C_6H_5; R′ = H) were we unable to prevent reduction to toluene, ethanedithiol, and other products, presumably because the second stage of reduction is considerably faster than the first in this instance.

In accordance with the previously postulated[1,7] mechanism, we assume that reduction of dithioacetals or -ketals proceeds *via* a two-stage electron transfer involving the dianion shown in Scheme III. The carbanion moiety is stabilized by the adjacent sulfur atom (d-orbital resonance) which may account for its reluctance to undergo further reduction as well as for the much higher yields generally achieved in the reduction of dithioacetals or -ketals to alkylthiomercaptans compared to the yields of alkoxy mercaptans previously obtained[1] from monothioacetals and -ketals.[6] Only when the carbanion formed in the second stage of cleavage (Scheme IV) is particularly stable, *e.g.*, when it is a methyl or

SCHEME IV



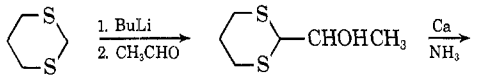
benzyl anion[6] or when it is inductively stabilized by an electron-withdrawing group (*e.g.*, R = $C_6H_5CH_2$), will overreduction occur readily.

The present procedure provides a convenient route to β- and γ-alkylthiomercaptans; its versatility is en-

(7) See also R. Gerdil and E. A. C. Lucken, *J. Chem. Soc.*, 2857, 544 (1963); 3916 (1964).

hanced by the availability of a wide variety of functionally 2-substituted 1,3-dithianes by the elegant procedure of Corey and Seebach.[8] Thus (last entry in Table I), the reduction of 2-(1-hydroxyethyl)-1,3-dithiane, synthesized from 1,3-dithiane and acetaldehyde,[8] produced 1-(3-mercaptopropylthio)-2-propanol (Scheme V) in 83% yield.

SCHEME V



$CH_3CHOHCH_2SCH_2CH_2CH_2SH$

The reduction of 2-isopropyl-1,3-dithiolane is described as typical of those in which an excess of calcium is employed. Additional experimental techniques, tables of starting materials and products, syntheses of authentic samples, and a more detailed discussion of the reaction mechanism are found in Part B.

Reduction of 2-Isopropyl-1,3-dithiolane.—To 300 ml of liquid ammonia in a 500-ml three-necked flask equipped with an addition funnel, mechanical stirrer, and venting tube was added 2.7 g (0.067 g-atom) of calcium turnings. When the metal had dissolved (5 min), a solution of 4.70 g (0.034 mol) of 2-isopropyl-1,3-dithiolane in 50 ml of anhydrous ether was added over a period of 5–10 min. After an additional 10 min, the excess calcium (blue solution) was destroyed by addition of solid ammonium chloride. The ammonia was allowed to evaporate in the hood and the residual slurry treated with 100 ml of 1 *N* hydrochloric acid. The layers were separated and the aqueous layer three times extracted with 50-ml portions of ether. The combined ether solution was dried over $MgSO_4$ and concentrated to give 4.57 g of an oil, a small aliquot of which was titrated with iodine for mercaptan content;[9] the remainder of the oil was distilled, bp 92° (15 mm), yield 4.04 g (85%). The infrared and nmr spectra were compatible with the assigned structure, $(CH_3)_2CHCH_2SCH_2CH_2SH$.

Part B

The starting 1,3-dithiolanes and 1,3-dithianes for this investigation were generally formed from the appropriate aldehydes or ketones and ethane-1,2-dithiol or propane-1,3-dithiol in the presence of an acid catalyst.[10] Properties and yields of starting materials are indicated in Table II. The yields in the reductions (Table I), usually determined by iodimetry[9] in duplicate reactions, generally exceeded 90% although in one run, involving *n*-heptyl mercaptan as the product, disulfide formation lowered the yield to 51%; the disulfide was readily reconverted to mercaptan by treatment with zinc amalgam in the presence of acid,[9] however.

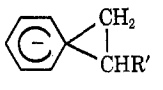
Reduction of the dithiolanes derived from formaldehyde, phenylacetaldehyde, phenylacetone, and benzaldehyde and of the dithiane derived from formaldehyde with excess calcium in ammonia led to double cleavage (Scheme II), the products being ethane-1,2-dithiol or propane-1,3-dithiol, respectively, and ethylbenzene, *n*-propylbenzene, and toluene (methane, presumably formed from the formyl derivatives, was not isolated). In the case of the formaldehyde, phenylacetaldehyde, and phenylacetone derivatives, it was established that hydrocarbon formation did, in fact, occur in two sequential steps (Scheme I followed by Scheme II), for not only could the desired single cleavage (Scheme I) be achieved by limiting the amount of calcium to 2 equiv per mole of starting thioacetal or -ketal, but in addition, the initial products, $CH_3SCH_2CH_2SH$ and $C_6H_5CH_2CH_2SCH_2CH_2SH$, were further reduced to $HSCH_2CH_2SH$ and (in the second case) $C_6H_5CH_2CH_3$ by treatment with 3 equiv of calcium in ammonia. Only in the case of the benzaldehyde derivative 2-phenyl-1,3-dithiolane did we fail to arrest the reduction at the intermediate stage, the only products isolated being toluene and ethane-1,2-dithiol in low yield (other, unidentified and more complex products are also formed). The last result confirms previous reports in the literature;[2,3a] it is well known that benzyl sulfides, the expected initial products according to Scheme I, are readily cleaved by metal–ammonia combinations, the benzyl group often serving as a protective group in such instances.

Overreduction of the formaldehyde and benzaldehyde derivatives is readily explained in terms of the high stability of the methyl and benzyl carbanions formed in the second stage of cleavage (Scheme IV). That similar stabilization accounts for the overreduction of the phenylacetaldehyde and phenylacetone derivatives (Schemes I, II, IV; R = $C_6H_5CH_2$; R′ = H or CH_3) was not immediately obvious, since only an inductive electron withdrawal by the benzyl group can be invoked as stabilizing the corresponding carbanions (Scheme IV). Alternative pathways in these cases were considered (Scheme VI). One of these (i) involves formation of a

SCHEME VI

(i) $C_6H_5CH_2CHR'SCH_2CH_2S^- \xrightarrow[-NH_3]{NH_2^-} C_6H_5C^-HCHR'SCH_2CH_2S^- \longrightarrow {}^-SCH_2CH_2S^- + C_6H_5CH{=}CHR' \xrightarrow[NH_3]{Ca} C_6H_5CH_2CH_2R' + {}^-SCH_2CH_2S^-$

(ii) Reduction occurring *via* Scheme IV with stabilization of the homobenzylic carbanion as a phenanion



R′ = H or CH_3

benzylic carbanion followed by an E2cB elimination to give the ethanedithiolate dianion and a styrene which is known to be further reduced to an alkylbenzene by metal–ammonia.[11] The other hypothesis (ii) provides for stabilization of the intermediate of Scheme IV as a phenanion.

Both alternatives were ruled out by a study of the reduction of the ethylene dithioketal of 1-phenyl-2-propanone-1,1,3,3,3-d_5, $C_6H_5CD_2COCD_3$. Reduction of the thioketal proceeded *without* loss of deuterium (as established by nmr spectroscopy) to give pentadeuterated $C_6H_5CD_2CH_2CD_3$. It is clear that pathway i, Scheme

(8) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965). See also D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, **33**, 300 (1968), and references there cited.

(9) D. P. Harnish and D. S. Tarbell, *Anal. Chem.*, **21**, 968 (1949).

(10) R. H. Jones, G. E. Lukes, and J. I. Bashour, U. S. Patent 2,690,988 (1954); *Chem. Abstr.*, **49**, 9868*d* (1955).

(11) C. B. Wooster and J. F. Ryan, *J. Amer. Chem. Soc.*, **56**, 1133 (1934).

TABLE II

STARTING MATERIALS (1,3-DITHIOLANES AND 1,3-DITHIANES)

Ethylene dithioacetal or dithioketal[l] of	Yield, %	Bp, °C (mm)	$n^{20}D$	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found
Formaldehyde[a]	94	77 (23)	1.5988				
Acetaldehyde[b]	81	75 (23)	1.5637	39.96	39.64	6.70	6.83
Propionaldehyde[c]	83	87 (21)	1.5496				
Isobutyraldehyde	84	84 (9)	1.5382	48.60	49.00	8.16	8.16
3-Pentanone	85	53 (0.7)	1.5331	51.80	51.84	8.69	8.66
Pinacolone	84	...[d]		54.49	54.71	9.15	9.11
n-Heptaldehyde[b]	84	100.5–101 (1.1)	1.5189	56.78	56.88	9.53	9.66
Cyclohexanone[e]	94	86.5 (1.2)	1.5664				
Benzaldehyde[b,f]	95	109.5 (0.7)	1.6368	59.29	58.81	5.53	5.53
Phenylacetaldehyde[b]	92	122 (0.7)	1.6159	61.17	61.45	6.16	6.38
Phenylacetone	91	108 (0.7)	1.6010	62.81	62.67	6.71	6.65
1-Phenylpentadeuteriopropanone	94	104 (0.3)	1.6001				
Hydrocinnamaldehyde	85	130 (0.5)	1.5994	62.81	62.80	6.71	6.71
Trimethylene dithioacetal or dithioketal[m] of							
Formaldehyde[g]	93	...[h]					
Isobutyraldehyde[i]	82	69.5 (1.2)	1.5435				
Cyclohexanone[j]	98	90 (0.3)[k]					

[a] D. T. Gibson, *J. Chem. Soc.*, 12 (1930), reports bp 61° (11 mm), $n^{15}D$ 1.5975. [b] Reported in ref 10 without physical constants. [c] S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964), report bp 68° (10 mm). [d] Solid, mp 61–62°. [e] E. E. Reid and A. Jelinek, *J. Org. Chem.*, **15**, 448 (1950), report bp 107° (5 mm), $n^{25}D$ 1.5650. [f] Reported by B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, **41**, 2671 (1963), without physical constants. [g] J. R. Meadow and E. E. Reid, *J. Amer. Chem. Soc.*, **56**, 2177 (1934), report mp 53.3°. [h] Solid, mp 52.5–53°. [i] S. Oae, W. Tagaki, and A. Ohno (footnote *c*) report bp 134° (35 mm). [j] H. Hauptmann and M. M. Campos, *J. Amer. Chem. Soc.*, **72**, 1405 (1950), report bp 148–148.5° (17 mm), mp 40.5–41.5°. [k] Solid, mp 39–40°. [l] Respective registry numbers follow: 4829-04-3, 5616-51-3, 6008-80-6, 26733-24-4, 26733-25-5, 26785-73-9, 6008-84-0, 177-16-2, 5616-55-7, 26785-74-0, 20137-72-8, 26733-30-2, 14505-46-5. [m] Respective registry numbers follow: 505-23-7, 6007-25-6, 180-96-1.

VI, would have led to $C_6H_5CHDCH_2CD_3$ (*via* $C_6H_5CD{=}CHCD_3$). Pathway ii should presumably have given rise to isopropylbenzene as well as *n*-propylbenzene in the reduction of the undeuterated analog 1-phenyl-2-propanone by protonation at the CH_2 group of the cyclic intermediate. Pathway ii was disproved still more convincingly by reduction of ethyl 2-phenylethyl-1-*d* sulfide, $C_2H_5SCHDCH_2C_6H_5$, with calcium in ammonia which gave 1-phenylethane-2-*d*, $C_6H_5CH_2CH_2D$, in 71% yield, the position of the deuterium being exclusively in the 2 position as shown by nmr spectroscopy. Reduction thus proceeded by the anion $C_6H_5CH_2CHD^-$ and not by the corresponding phenanion (Scheme VI, ii, R = D) which should have produced nearly equal amounts of $C_6H_5CH_2CH_2D$ and $C_6H_5CHDCH_3$.

The method here described provides a much more convenient route to β- and γ-alkylthiomercaptans than known procedures: the slow addition of hydrogen sulfide to vinyl sulfides under pressure,[12] the conversion of β- or γ-hydroxy sulfides[13,14a] to chlorides and thence to mercaptans by treatment with NaSH,[14] or the reaction of mercaptans with thiiranes.[15] The last method was used here to obtain a comparison sample of 2-cyclohexylthioethanethiol in only 34% yield, contaminated with a considerable amount of oligomeric material. An authentic sample of $CH_3CHOHCH_2SCH_2CH_2CH_2SH$ (*cf.* Scheme V) was prepared in 36% yield from 1,3-propanedithiol and propylene oxide in the presence of sodium hydroxide.[16]

(12) M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 447 (1954).

(13) E. L. Eliel, L. A. Pilato, and V. G. Badding, *J. Amer. Chem. Soc.*, **84**, 2377 (1962).

(14) (a) S. E. Livingstone, *J. Chem. Soc.*, 437 (1956). NaSH is erroneously called "sodium ethyl sulphide" in this paper. (b) R. C. G. Moggridge, *ibid.*, 1105 (1946); L. J. Goldsworthy, G. F. Harding, W. L. Norris, S. G. P. Plant, and B. Selton, *ibid.*, 2177 (1948).

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Experimental Section

Melting points, determined on a Kofler block, and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord instrument. Nuclear magnetic resonance spectra were recorded with a Varian Associates Model V-4311 HR-60 spectrometer at 60 MHz by Mr. D. Schifferl. Carbon tetrachloride was used as solvent, with tetramethylsilane as an internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Starting Materials.—1,3-Dithiolane, 2-methyl-1,3-dithiolane, and 1,3-dithiane were prepared by the method of Corey and Seebach.[8] Dimethoxymethane or acetaldehyde was allowed to react with the appropriate dimercaptan with boron trifluoride etherate as catalyst. The remaining 1,3-dithiolanes and 1,3-dithianes were prepared by the method of Jones, *et al.*,[10] employing the appropriate dimercaptan, aldehyde, or ketone, except for phenylacetaldehyde, where the dimethyl acetal was used, and *p*-toluenesulfonic acid as catalyst. The yields and physical properties of starting materials are listed in Table II. Known starting materials agreed in their physical properties with samples previously prepared and described in the literature.

Reductions.—The reduction of 2-isopropyl-1,3-dithiolane has been described above as typical of reductions employing method A (see Table I), where mercaptan is the sole product, the reduction of 2-benzyl-1,3-dithiolane is described as typical of reductions employing method A (see Table I), where hydrocarbon is also isolated, and the reduction of 2-benzyl-2-methyl-1,3-dithiolane with a limited amount of calcium is described as typical of reductions employing method B (see Table I). Yields of reduction products are listed in Table I and their properties in Table III. Known reduction products agreed in their physical properties with samples previously prepared and described in the literature.

(16) *Cf.* R. D. Schuetz, *ibid.*, **73**, 1881 (1951).

TABLE III

REDUCTION PRODUCTS (β- AND γ-ALKYLTHIOMERCAPTANS)

R in $RSCH_2CH_2SH$[d]	Bp, °C (mm)	$n^{20}D$	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found
Methyl[a]	69.5 (26)	1.5409				
Ethyl[b]	92.5–93 (41)	1.5264				
n-Propyl[c]	95 (24)	1.5175				
Isobutyl	92 (15)	1.5084	47.95	48.29	9.39	9.38
3-Pentyl	57 (0.4)	1.5087	51.16	51.04	9.81	9.93
3,3-Dimethyl-2-butyl	68 (0.9)	1.5059	53.87	53.64	10.17	10.06
n-Heptyl	95 (0.7)	1.5001	56.19	56.17	10.48	10.68
Cyclohexyl	85 (0.6)	1.5420	54.49	54.72	9.15	8.99
2-Phenylethyl	114.5 (0.5)	1.5847	60.55	60.82	7.11	7.23
1-Phenyl-2-propyl	117 (0.7)	1.5735	62.21	62.39	7.59	7.81
3-Phenyl-1-propyl	130.5 (0.4)	1.5747	62.21	62.15	7.59	7.70
R in $RSCH_2CH_2CH_2SH$[e]						
Methyl	79 (18)	1.5278	39.30	39.60	8.25	8.36
Isobutyl	73 (1.5)	1.5028	51.16	51.07	9.81	9.87
Cycohexyl	100.5 (0.7)	1.5347	56.78	56.97	9.53	9.55

[a] E. M. Meade and F. N. Woodward, *J. Chem. Soc.*, 1894 (1948), report bp 82° (40 mm). [b] Reference 12 reports bp 60° (9 mm), $n^{20}D$ 1.5273. [c] L. J. Goldsworthy, G. F. Harding, W. L. Norris, S. G. P. Plant, and B. Selton, *J. Chem. Soc.*, 2177 (1948), report bp 75–77° (11 mm). [d] Respective registry numbers follow: 22322-43-6, 26750-44-4, 26733-37-9, 10160-80-2, 26718-03-6, 26718-04-7, 26718-05-8, 10160-81-3, 26785-75-1, 26718-07-0, 26718-08-1. [e] Respective registry numbers follows: 26718-09-2, 26718-10-5, 26718-11-6.

Reduction of 2-Benzyl-1,3-dithiolane with Calcium in Ammonia. Method A.—By the procedure described in Part A above, 6.09 g (0.031 mol) of 2-benzyl-1,3-dithiolane in 50 ml of ether was treated with 4.5 g (0.11 g-atom) of calcium in 300 ml of liquid ammonia; then ammonium chloride was added to destroy excess calcium. After the ammonia had evaporated, the resulting slurry was acidified with 150 ml of 2 *N* hydrochloric acid. The layers were separated; the aqueous layer was extracted three times with 50-ml portions of ether. The combined ether solutions were extracted four times with 40-ml portions of 2 *N* potassium hydroxide. The ether solution was dried over anhydrous magnesium sulfate and concentrated to give a clear colorless oil. Distillation afforded 2.34 g (71%) of ethylbenzene, bp 134.5–135° (755 mm), having an infrared spectrum identical with that of an authentic sample. The combined basic extracts were acidified with 90 ml of 5 *N* hydrochloric acid and extracted three times with 50-ml portions of ether. The combined ether solutions were dried over anhydrous magnesium sulfate and partially concentrated to give 4.03 g of a clear yellow oil. A small aliquot of this oil was removed and titrated for mercaptan content with iodine;[9] the yield of mercaptan was 97%. The remainder was distilled to give 2.06 g (71%) of 1,2-ethanedithiol, bp 42.5° (15 mm), having an infrared spectrum identical with that of an authentic sample.

Method B.—To 300 ml of liquid ammonia contained in the apparatus described above was added 6.31 g (0.030 mol) of 2-benzyl-2-methyl-1,3-dithiolane in 50 ml of anhydrous ether. Then, 1.31 g (0.033 g-atom)[17] of calcium turnings was added as quickly as possible (*ca.* 2 min). The ammonia was allowed to evaporate and the residual slurry was treated with 100 ml of 1 *N* hydrochloric acid. The layers were separated and the acidic aqueous layer extracted three times with 50-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and concentrated to give a clear yellow oil. Distillation afforded 5.79 g (91%) of 2-(1-phenyl-2-propylthio)ethanethiol, bp 117° (0.7 mm). The infrared and nmr spectra were compatible with the assigned structure.

Reduction of 2-Phenyl-1,3-dithiolane (Method B).—The reduction of 5.47 g (0.03 mol) of 2-phenyl-1,3-dithiolane was effected as described in the previous experiment. The solution turned black, the color changing to brown during the evaporation of the ammonia. The product was separated into neutral and acidic fractions as indicated under method A above. The neutral fraction weighed 2.26 g and yielded *ca.* 0.5 g (18%) of toluene, bp 110° (750 mm) upon distillation; its infrared spectrum was identical with that of an authentic sample. The acidic material was a red oil weighing 3.85 g. Distillation afforded *ca.* 0.45 g (16%) of 1,3-ethanedithiol, bp 59.5–60.5° (34 mm), whose infrared spectrum was identical with that of an authentic sample. The remaining material (2.65 g) distilled with much difficulty and some decomposition at 100–200° (0.5 mm) and yielded 0.33 g of sulfur and 1.75 g of an unidentified semisolid material which was not extractable into aqueous potassium hydroxide.

Deuteration of Phenylacetone.—Phenylacetone (25 g) was treated with 10 g of anhydrous potassium carbonate in 100 g of deuterium oxide at reflux for 24 hr.[18] After cooling, the reaction mixture was extracted with three 50-ml portions of ether, previously saturated with deuterium oxide. The combined ether solutions were dried over anhydrous magnesium sulfate and concentrated to give 24.6 g of a clear yellow oil. Distillation afforded phenylpentadeuteriopropanone: bp 100° (15 mm); yield 21.8 g (84%); nmr spectrum multiplet 109.5–121.5 Hz (0.24 H) (3 H in undeuterated compound, hence 92% D at C-3), multiplet 206.5–213.5 Hz (0.20 H) (2 H in undeuterated compound, hence 90% D at C-1), multiplet 418–441 Hz (5 H).

Reduction of Ethylene Dithioketal of 1-Phenyl-2-propanone-1,1,3,3,3-d_5. A.—To a solution of 5.51 g (0.04 mol) of phenylpentadeuteriopropanone and 4.15 g (0.044 mol) of 1,2-ethanedithiol in 80 ml of benzene was added *ca.* 50 mg of *p*-toluenesulfonic acid and the mixture refluxed for 2 hr, water being removed azeotropically by means of a Dean and Stark trap.[10] The reaction mixture was cooled and poured into a solution of sodium carbonate in deuterium oxide. The basic solution was extracted three times with 50-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, concentrated, and distilled to give the ethylene dithioketal of phenylpentadeuteriopropanone, bp 104° (3 mm), yield 8.0 g (94%). The infrared spectrum was compatible with the assigned structure. Nmr spectrum: broad singlet 92.5 Hz (0.62 H) (3 H in undeuterated species, hence 79% D at C-3), multiplet 167–203.5 Hz (4.64 H; 0.64 H attributed to C_1 position) (6 H in undeuterated species, hence 68% D at C-1), multiplet 420–444.5 Hz (5 H).

B.—The ethylene dithioketal of phenylpentadeuteriopropanone was reduced and the reaction mixture worked up according to the procedure for 2-methyl-2-benzyl-1,3-dithiolane (method A). Distillation of the neutral fraction afforded 1-phenylpropane-1,1,3,3,3-d_5: bp 55.5° (20 mm); nmr spectrum multiplet at 38.5–63 Hz (0.63 H) (3 H in undeuterated species, hence 79% D at C-3), broad singlet at 90.5 Hz (2 H), multiplet at 137–160.5 Hz (0.59 H) (2 H in undeuterated species, hence 70% D at C-1), singlet at 424.5 Hz (5 H).

Reduction of 2-(2-Phenylthio)ethanethiol and 2-Methylthioethanethiol.—The conditions of method A were used, starting with 5.95 g (0.030 mol) of $C_6H_5CH_2SCH_2CH_2SH$ and employing an excess of calcium (*ca.* 1.97 g, 0.049 g-atom). The work-up was as in method B (partition between ether and aqueous KOH).

(17) To determine the optimum amount of calcium to be used, 5.23 g (0.030 mol) of 2-cyclohexyl-1,3-dithiolane was similarly treated, adding small portions of calcium, slowly, till a permanent blue color resulted. This required 1.31 g of calcium, thus a 10% excess of Ca seems desirable.

(18) A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, **85**, 3747 (1963).

The neutral fraction, upon distillation, afforded 2.08 g (65%) of ethylbenzene, bp 134–135° (745 mm), whose infrared spectrum was identical with that of an authentic sample. The acidic fraction, 4.11 g of a yellow oil, was shown by iodine titration[9] to contain 93% of mercaptan calculated as 1,2-ethanedithiol. Distillation gave 2.45 g (86%) of ethanedithiol, bp 59° (33 mm), identified by infrared spectrum.

Similar reduction of 2.74 g (0.025 mol) of $CH_3SCH_2CH_2SH$ with 1.61 g of calcium yielded 94% of mercaptan,[9] isolated in 79% yield [1.98 g, bp 59.5–60° (34 mm)] identified as 1,2-ethanedithiol by infrared spectrum.

2-Phenylethyl-1-*d* *p*-Toluenesulfonate.—2-Phenylethanol-1-*d* was prepared by LAD reduction of the aldehyde[19] in 95% yield: bp 67° (0.6 mm); $n^{20}D$ 1.5317 [lit.[19] bp 55–57° (0.7 mm), $n^{20}D$ 1.5315)]; nmr spectrum doublet at 160 Hz (J = 7 Hz, 2 H), triplet at 214.5 Hz (J = 7 Hz, 1 H), singlet at 224.5 Hz (1 H), singlet at 425.5 Hz (5 H). The *p*-toluenesulfonate was prepared in the usual manner[19–21] from 10 g of *p*-toluenesulfonyl chloride dissolved in 15 ml of pyridine added to 5.45 g of the alcohol in 10 ml of pyridine at −10°. The mixture was left at 0° for 3 hr before work-up and yielded 10.94 g (89%) of the *p*-toluenesulfonate: mp 38–40° (lit.[19] 38–40°); nmr spectrum 138.5 Hz (s, 3 H), 169 Hz (d, J = 7 Hz, 2 H), 244.5 Hz (t, J = 7 Hz, 1 H), multiplet at 406.5–469 Hz (9 H).

Ethyl 2-Phenyl-1-monodeuterioethyl Sulfide.—A solution of 10.0 g (0.036 mol) or 2-phenyl-1-monodeuterioethyl tosylate in 20 ml of ether was treated with 45 ml of 6 N sodium hydroxide and 8.5 g (0.14 mol) of ethyl mercaptan at 25°, with constant stirring under nitrogen for 70 hr.[22] A further quantity of 7 g (0.11 mol) of ethyl mercaptan was then added and the reaction continued for an additional 50 hr. After the addition of 20 ml of water, the product was extracted with three 50-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated. By treatment with hexane, the crude product was divided into a hexane-soluble and a hexane-insoluble fraction. From the latter, by purification on neutral alumina, was obtained 4.37 g (44%) of unreacted tosylate. Distillation of the hexane-soluble extract afforded 2.51 g (42%) of the sulfide: bp 80° (0.8 mm); $n^{20}D$ 1.5411 [lit.[23] for the undeuterated species, bp 92–94° (3 mm); $n^{20}D$ 1.5420]; nmr spectrum 72 Hz (t, J = 7.5 Hz, 3 H), 146.5 Hz (q, J = 3.5 Hz, 2 H), 155–178 Hz (multiplet, 3 H), 427 Hz (s, 5 H).

Reduction of Ethyl 2-Phenyl-1-deuterioethyl Sulfide with Calcium in Ammonia.—Using method A, 1.67 g (0.01 mol) of $C_6H_5CH_2CHDSC_2H_5$ was reduced with 0.5 g (0.013 g-atom) of calcium in 100 ml of ammonia to give 0.76 g (71%) of 1-phenylethane-2-*d*: bp 44° (27 mm); $n^{20}D$ 1.4948; nmr spectrum 70 Hz (triplet of triplets, J_1 = 7.5 Hz, J_2 = 2 Hz, 2 H), 152.5 Hz (t, J = 7.5 Hz, 2 H), 425.5 Hz (s, 5 H).

Reduction of 2-Heptyl-1,3-dithiolane with Calcium in Ammonia.—Using method A, 2.87 g (0.015 mol) of 2-hexyl-1,3-dithiolane was reduced with 3.0 g (0.075 g-atom) of calcium in 300 ml of ammonia to give 2.84 g of semisolid crude material. A small aliquot (*ca.* 0.1 g) was removed and titrated for mercaptan content with iodine.[9] The yield of mercaptan was 51%. A similar aliquot was then removed and dissolved in 20 ml of absolute ethanol with 0.5 ml of 10 N hydrochloric acid and treated with 2 g of zinc amalgam. The decanted solution was again titrated for mercaptan content with iodine,[9] the yield of mercaptan now being 94%.

2-(1-Hydroxyethyl)-1,3-dithiane.[8]—To a solution of 7.25 g (0.060 mol) of 1,3-dithiane in 200 ml of tetrahydrofuran at −30°, stirred under nitrogen, was added 48 ml (0.061 mol) of a 1.27 M solution of *n*-butyllithium in hexane, at the rate of 2 ml/min. A clear yellow solution was obtained. After stirring for 1.5 hr at −30°, the solution was allowed to warm to −5°, 3.3 g (0.075 mol) of acetaldehyde was added, and the mixture was stirred for 14 hr at 0°, under nitrogen. It was then poured into 750 ml of water, acidified to pH 5–6, and extracted with five 150-ml portions of ether. The combined extracts were washed once with 50 ml of 2 N potassium hydroxide and dried over anhydrous magnesium sulfate, and the solvents evaporated to give 9.11 g of a clear yellow oil. Treatment with hexane afforded 8.15 g of a hexane-insoluble fraction and 0.6 g of a hexane-soluble fraction. From the latter was isolated *ca.* 0.4 g (6%) of unreacted 1,3-dithiane. Distillation of the hexane-insoluble fraction gave an additional 0.2 g (3%) of 1,3-dithiane and 6.39 g (65%) of crude 2-(1-hydroxyethyl)-1,3-dithiane, bp 90–98° (0.4 mm). The product was redistilled to afford 4.8 g of the pure material: bp 93° (0.55 mm); $n^{20}D$ 1.5759; nmr spectrum 79.5 Hz (d, J = 6 Hz, 3 H), 99.5–145 Hz (multiplet, 2 H), 145–183.5 Hz (multiplet, 4 H), 186 Hz (s, 1 H), 220.5–252.5 Hz, (multiplet, 2 H).

Anal. Calcd for $C_6H_{12}OS_2$: C, 43.86; H, 7.37. Found: C, 43.82; H, 7.51.

1-(3-Mercaptopropylthio)-2-propanol. 1.—Using method A, 2.40 g (0.015 mol) of 2-(1-hydroxyethyl)-1,3-dithiane was reduced with 0.8 g (0.02 g-atom) of calcium in 150 ml of ammonia to give 2.69 g of crude 1-(3-mercaptopropylthio)-2-propanol; yield by iodine titration,[9] 91%. Distillation afforded 2.00 g (83%) of pure product: bp 99.50 (0.6 mm); $n^{20}D$ 1.5318; nmr spectrum 72.5 Hz (d, J = 6 Hz, 3 H), 78.5 Hz (t, J = 7.5 Hz, 1 H), 94.5–126 Hz (multiplet, 2 H), 140.5–173 Hz (multiplet, 6 H), 204 Hz (s, 1 H), 228 Hz (sextet, J = 6 Hz, 1 H).

2.—To 21.7 g (0.2 mol) of 1,3-propanedithiol was added 1.0 g of 30% sodium hydride in mineral oil, under nitrogen, with stirring, at 25°. The mixture was cooled to 0° and 17 ml (0.24 mol) of propylene oxide added over 1 hr.[16] Stirring was continued for an additional hr at 0°, and then the reaction mixture acidified with 3% hydrochloric acid. The product was extracted with two 50-ml portions of ether and the combined ether extracts were washed with three 20-ml portions of water and then dried over anhydrous magnesium sulfate. The ether was removed and distillation gave 5.87 g (22%) of unreacted 1,3-propanedithiol, bp 77–78° (23 mm), and 14.1 g of a second fraction, bp 115–128° (0.8 mm). Some higher boiling material (6.54 g) remained. A solution of the second fraction in 100 ml of ether was extracted with three 50-ml portions of 5 N potassium hydroxide solution. The combined extracts were acidified with 200 ml of 5 N hydrochloric acid and extracted with three 100-ml portions of ether. After drying over anhydrous magnesium sulfate, concentration yielded 12.1 g (36%) of crude 1-(3-mercaptopropylthio)-2-propanol. Distillation afforded 11.5 g (34%) of the pure product, bp 99° (0.5 mm), $n^{20}D$ 1.5321, having infrared and nmr spectra identical with those for the product obtained above.

Anal. Calcd for $C_6H_{12}OS_2$: C, 43.33; H, 8.48. Found: C, 43.11; H, 8.56.

2-(Cyclohexylthio)ethanethiol.—To a solution of 9.9 g (0.085 mol) of cyclohexyl mercaptan in alcoholic sodium ethoxide (1.6 g of sodium and 75 ml of ethanol) at 0° was added, dropwise, 3.3 g (0.055 mol) of ethylene sulfide at −10°. The reaction mixture was allowed to warm to 25° over a period of 40 min, 250 ml of 5% acetic acid then added, and the product extracted with three 50-ml portions of anhydrous ether. After drying over anhydrous magnesium sulfate, concentration left 12.9 g of an oil. Distillation afforded 4.48 g (46%) of crude 2-(cyclohexylthio)ethanethiol, bp 71–78° (0.08 mm). Redistillation gave 3.3 g (34%) of purer material, bp 84–85° (0.5 mm), $n^{20}D$ 1.5419, whose infrared spectrum was identical with that of the product prepared from the calcium–ammonia reduction of 2-cyclohexyl-1,3-dithiolane.

Registry No.—2-Phenylethyl-1-*d* *p*-toluenesulfonate, 26718-12-7; ethyl 2-phenyl-1-monodeuterioethyl sulfide, 26785-76-2; 1-phenylethane-2-*d*, 1861-04-7; 2-(1-hydroxyethyl)-1,3-dithiane, 14947-48-7; 1-(3-mercaptopropylthio)-2-propanol, 26718-15-0; 2-(cyclohexylthio)-ethanethiol, 10160-81-3.

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