TABLE IV

MASS SPECTRA OF DEUTERATED MATERIALS

m/e	Va	VIa	Vb	VIb	VIIb
27	23.16	22.73	12.94	12.84	17.66
39	11.69	11.70	17.54	16.85	21.53
41	16.20	16.13	36.45	35.38	41.23
43	7.98	7.75	41.98	41.72	14.93
44	7.18	7.11	7.23	6.99	48.96
45	15.41	15.60	12.32	12.92	6.79
55	13.53	13.62	21.83	21.43	39.23
56	11.28	11.42	24.37	24.21	7.66
57	4.95	4.33	7.82	7.33	100
58	70.80	71.89	100	100	21.77
67	2.81	2.78	4.25	4.02	11.99
82	4.16	4.21	6.63	6.39	25.04
83	10.45	10.49	23.72	23.52	58.13
84	9.59	9.81	55.30	54.72	5.10
85	4.72	3.85	4.35	4.92	0
86	100	100	...	...	...
100	10.30	10.41	64.70	62.08	73.92

Reduction of Cyclohexanone Ethylene Ketal.—The reduction of 5.68 g. (0.04 mole) of this ketal with 0.84 g. (0.02 mole) of lithium aluminum deuteride and 10.66 g. (0.08 mole) of aluminum chloride in anhydrous ether was carried out according to the general procedure described earlier except that the deuteride was added as an ether suspension rather than as a standard solution. The yield of 2-cyclohexyloxyethanol-*d*, b.p. 100° (12 mm.), $n^{20}D$ 1.4629, was 5.07 g. (88%). For purposes of analysis, this sample was transformed into 2-cyclohexyloxy-1-chloroethane in the way described above for the higher (undeuterated) homolog. The chloride, obtained in 78% yield, boiled at 94° (12 mm.), $n^{20}D$ 1.4633, and was reduced to deuterated cyclohexyl ethyl ether, b.p. 70–80° (55 mm.), $n^{20}D$ 1.4302, by means of lithium aluminum hydride in tetrahydrofuran. The product was purified by gas chromatography and then submitted to mass spectrometry. The mass spectrum is shown in Table IV (sample Va). Mass spectrometry at reduced ionizing voltage indicated 97.6% monodeuteration for Va. It is clear from Table IV that Va is identical with VIa (cyclohexyl-1-*d* ethyl ether).

Reduction of Cyclohexanone Trimethylene Ketal.—This experiment was carried out in the same way as that for the lower homolog described above. 3-Cyclohexyloxy-1-propanol-*d*, b.p. 66° (0.3 mm.), $n^{20}D$ 1.4620, was obtained in 91% yield and was converted to the chloride, b.p. 96° (11 mm.), $n^{20}D$ 1.4622, in 78% yield. The chloride, in turn, was reduced to deuterated cyclohexyl *n*-propyl ether, b.p. 58° (10 mm.), $n^{20}D$ 1.4351 (sample designated as Vb) in 52% yield. The sample was purified by gas chromatography prior to mass spectrometry; isotopic purity 97.3%. The mass spectrum, shown in Table IV, clearly indicates that the reaction product Vb is cyclohexyl-1-*d* *n*-propyl ether (VIb) and not cyclohexyl *n*-propyl-3-*d* ether (VIIb), which latter compound was absent in Vb. Infrared spectroscopy confirmed this conclusion: both Vb and VIb have characteristic bands at 1390 and 820 cm.$^{-1}$; the characteristic bands of VIIb at 1370 and 850 cm.$^{-1}$ were absent in Vb.

Acknowledgment.—Our work in the area of hydride reductions has been aided by a grant from Merck and Co., Inc.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AND RADIATION LABORATORY[1] OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Reductions with Metal Hydrides. XIII. Hydrogenolysis of Hemithioacetals and Hemithioketals with Lithium Aluminum Hydride–Aluminum Chloride[1]

BY ERNEST L. ELIEL, LOUIS A. PILATO AND VICTOR G. BADDING

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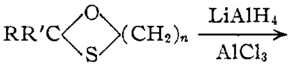
The reduction of cyclic hemithioacetals and hemithioketals with lithium aluminum hydride–aluminum chloride leads to β-hydroxyethyl and γ-hydroxypropyl sulfides, usually in excellent yields. Carbon–oxygen cleavage occurs to the exclusion of carbon–sulfur cleavage. Upon prolonged reaction with the "mixed hydride," further hydrogenolysis of the β-hydroxyethyl sulfide function to an ethyl sulfide function takes place. Tracer studies indicate that this hydrogenolysis proceeds *via* a cyclic sulfonium ion. Both the hydroxyalkyl sulfides and the alkyl sulfides have been transformed into a variety of other products. The mixed hydride reduction serves as a novel and convenient synthesis of thioethers from aldehydes and ketones: $RR'CO \rightarrow RR'CHSCH_2CH_2X$ where $X = OH$, H or CH_2OH.

In the previous paper,[2] the hydrogenolysis of acetals and ketals to hydroxyethers by "mixed hydride"[3] (lithium aluminum hydride–aluminum chloride in a 1:4 ratio) in ether solution was described. This method has now been extended to hemithioacetals and hemithioketals. In all cases, cleavage of the carbon–oxygen bond occurred exclusively (eq. i), the carbon–sulfur bond remaining intact, as evidenced by the absence of base-soluble mercaptans among the reaction products



$RR'CHS(CH_2)_nOH \quad n = 2 \text{ or } 3$ (i)

The compounds reduced and yields of reduction products are shown in Table I.

In most instances, the yields of hydroxysulfides are excellent. In the few cases where yields were low, this was traced to further hydrogenolysis of the β-hydroxyethyl sulfides to ethyl sulfides[4] (eq. ii)

$$RR'CHSCH_2CH_2OH \xrightarrow[AlCl_3]{LiAlH_4} RR'CHSCH_2CH_3 \quad \text{(ii)}$$

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[1] The Radiation Laboratory is operated under contract with the Atomic Energy Commission. This paper is taken in part from the Ph.D. dissertations of Louis A. Pilato and Victor G. Badding; for a preliminary report, see *J. Am. Chem. Soc.*, **81**, 6087 (1959).

[2] E. L. Eliel, V. G. Badding and M. N. Rerick, *ibid.*, **84**, 2371 (1962).

[3] E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961).

(4) Hydrogenolysis of the alcohol function may sometimes be minimized by avoiding an excess of mixed hydride. Thus the difference in yield of *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl sulfide from the two diastereoisomeric 4-*t*-butylcyclohexanone ethylene hemithioketals (Table I) is undoubtedly occasioned by the fact that a larger excess of hydride (leading to more hydrogenolysis) was used with the liquid isomer than with the solid. When the same large excess (200%) was used with the solid isomer, 21% of the ethyl thioether resulted along with 77% of the β-hydroxyethyl thioether. In some instances, however, quite extensive hydrogenolysis seems to be unavoidable because it occurs at a rate comparable to that of the primary hemithioketal cleavage. A case in point is the ethylene hemithioketal of camphor (Table I). The causes responsible for this are not yet completely understood.

TABLE I

REDUCTION OF HEMITHIOACETALS AND HEMITHIOKETALS WITH LITHIUM ALUMINUM HYDRIDE–ALUMINUM CHLORIDE (EQ. i)

2-hour reflux time, 100% excess hydride

R	R′	*n*	Yield, %
CH_3	CH_3	2	83
n-C_6H_{13}	H	2	74
n-C_6H_{13}	CH_3	2	79
C_6H_5	H	2	88
C_6H_5	CH_3	2	79
Cyclohexylidene		2	91
4-Methylcyclohexylidene[a]		2	80
4-*t*-Butylcyclohexylidene[b]		2	66[c,d]
4-*t*-Butylcyclohexylidene[e]		2	80[c,f]
3-Cholestanylidene[g]		2	80[h]
2-Bornylidene[i]		2	14[i,j]
C_6H_5	H	3	98
Cyclohexylidene		3	91

[a] Mixture of diastereoisomers. [b] Isomer m.p. 1–2°. [c] *trans* isomer. [d] 200% excess of hydride; also obtained 26% of *trans*-4-*t*-butylcyclohexyl ethyl thioether. [e] Isomer m.p. 74–75°. [f] Also obtained 6% of *trans*-4-*t*-butylcyclohexyl ethyl thioether. [g] Isomer m.p. 135–136°. [h] Also obtained 9% 3-cholestanyl ethyl sulfide (probably both this and the hydroxysulfide are β). [i] From camphor, stereochemistry unknown. [j] Also 70% of the corresponding ethyl sulfide.

By employing longer reaction times, this further reduction can often be brought about deliberately so that the major reduction products of the hemithioketals may be ethyl thioethers. Pertinent data are shown in Table II.

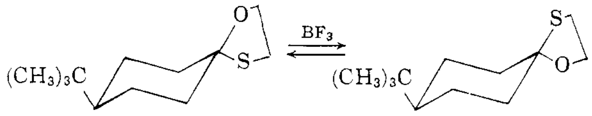
TABLE II

FURTHER HYDROGENOLYSIS IN REDUCTION OF HEMITHIOKETALS

R	R′	*t*, hr.[a]	Yield, % RR′CHS-CH_2CH_2OH	Yield, % RR′CHS-CH_2CH_3
n-C_6H_{13}	H	20	34	34
n-C_6H_{13}	CH_3	10	32	32
C_6H_5	H	24	86	Trace
C_6H_5	CH_3	4	73	7
Cyclohexylidene		8	60	28
		24	20	63
4-*t*-Butylcyclohexylidene[b]		24	46[c]	37[c]
4-*t*-Butylcyclohexylidene[d]		16	50[c]	37[c]
3-Cholestanylidene[e]		30	Trace	69
2-Bornylidene[f]		12	None	81[f]

[a] Reflux time, hours. [b] Isomer m.p. 1–2°. [c] *trans* isomer. [d] Isomer m.p. 74–75°. [e] Isomer m.p. 112–113°. [f] Stereochemistry unknown.

Starting Materials.—The starting hemithioacetals and hemithioketals (1,3-oxathiolanes and 1,3-oxathianes) required in the synthesis described are prepared in high yield from the corresponding aldehydes and ketones and appropriate hydroxymercaptan in the presence of an acid catalyst.[5–7] Whereas β-hydroxyethyl mercaptan is commercially available,[8] γ-hydroxypropyl mercaptan is accessible only through a somewhat tedious synthesis.[9] Table III (Experimental) lists all starting materials prepared in the present investigation. Of special interest are the hemithioketals of 4-*t*-butylcyclohexanone and 3-cholestanone which were each obtained in two pure diastereoisomeric forms. 3-Cholestanone has been previously converted[7,10] to a hemithioketal m.p. 135–136° assigned[7b] the C–S (β) configuration. We obtained the same material (both with the above melting point and in an isomorphic form, m.p. 144–145°) as the major product of the reaction of 3-cholestanone with β-mercaptoethanol, but, in addition, isolated an isomeric material, m.p. 112–113°, by chromatography of the mother liquors. Similarly, 4-*t*-butylcyclohexanone gave two ethylenehemithioketals separated by column chromatography, one melting at 1–2° and the other melting at 74–75°. Tentative assignment of configuration was made on the basis of n.m.r. spectra. *cis*-4-*t*-Butylcyclohexyl methyl ether shows the protons of the (axial) ether methyl group at −193 c.p.s., whereas the *trans* isomer shows the (equatorial) ether methyl protons at −195 c.p.s., *i.e.*, at lower field.[11] Now the liquid hemithioketal from 4-*t*-butylcyclohexanone has the OCH_2 signal at −243 c.p.s., whereas the solid epimer has it at the lower field value of −245 c.p.s. It may, therefore, be tentatively concluded that the solid isomer has equatorial oxygen (and therefore axial sulfur), whereas the liquid isomer has axial oxygen and equatorial sulfur (Fig. 1). The resonance signals for the SCH_2 groups are consistent with this assignment, that of the solid isomer coming at the higher field value of −175 c.p.s. and that of the liquid isomer being at the lower field value of −177 c.p.s.[12] Similar assignment to the 3-cholestanone hemithioketals leads to the tentative conclusion that the isomer m.p. 112–113° has equatorial oxygen and axial sulfur, whereas the previously known higher melting isomer has axial (α) oxygen and equatorial (β) sulfur, in agreement with the assignment previously made[7b].



I, m.p. 1–2°
CH_2O −243 c.p.s.
CH_2S −177 c.p.s.

II, m.p. 74–75°
CH_2O −245 c.p.s.
CH_2S −175 c.p.s.

Fig. 1.—4-*t*-Butylcyclohexanone ethylene hemithioketals.

Treatment of either solid or liquid 4-*t*-butylcyclohexanone hemithioketal with excess boron trifluoride etherate in ether led to fairly rapid equilibration to an approximately 50–50 mixture (Fig. 1). When only a catalytic amount of boron trifluoride was employed, equilibration was much slower (taking approximately six months at room temperature) and led to an equilibrium mixture containing 58% of the solid isomer and 42%

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(5) E. J. Salmi, *Ber.*, **71B**, 1803 (1938).

(6) F. Kipnis and J. Ornfelt, *J. Am. Chem. Soc.*, **71**, 3555 (1949).

(7) (a) C. Djerassi and M. Gorman, *ibid.*, **75**, 3704 (1953); (b) C. Djerassi, M. Shamma and T. Y. Kan, *ibid.*, **80**, 4723 (1958).

(8) Kindly donated by Union Carbide, Inc.

(9) R. O. Clinton, C. M. Suter, S. C. Laskowski, M. Jackman and W. Huber, *J. Am. Chem. Soc.*, **67**, 594 (1945).

(10) L. F. Fieser, *ibid.*, **76**, 1945 (1954).

(11) M. Gianni, unpublished observations. For a similar observation *cf.* R. U. Lemieux, R. K. Kullnig, and R. Y. Moir, *J. Am. Chem. Soc.*, **80**, 2237 (1958).

(12) All shifts are reported at 60 mc. from tetramethylsilane as zero. The relative assignments of OCH_2 and SCH_2 are based on precedents in the literature; *e.g.*, $(CH_3CH_2)O$, −202 c.p.s.; $(C_2H_5CH_2)_2S$, −143 c.p.s.: G. Van Dyke Tiers, "Tables of τ-Values," Minnesota Mining and Manufacturing Co., St. Paul, Minn.

of the liquid isomer, suggesting, surprisingly, that the epimer with axial sulfur is thermodynamically slightly preferred over that with axial oxygen.[13] Equilibration of the 3-cholestanone ethylene hemithioketals with excess boron trifluoride also leads to an approximately 50:50 mixture of the epimers.[14]

Of the other hemithioketals prepared here, only that derived from 4-methylcyclohexanone and that derived from camphor can exist in diastereoisomeric forms. In neither case were two isomers isolated, but in the 4-methylcyclohexanone derivative, evidence for their presence was obtained from the doubling of the OCH_2 and SCH_2 signals in the n.m.r. spectrum. In the case of camphor, it is not now known whether only one epimer or a mixture of two epimers was formed in the hemithioketalization.

Products.—The physical properties of the products obtained in this investigation are summarized in Table IV (Experimental). A few of the products are known and their physical properties corresponded to those in the literature. In other cases, authentic comparison materials were synthesized from halides or tosylates and mercaptides. Of special interest is the reaction of *cis*-4-*t*-butylcyclohexyl tosylate and sodium β-hydroxyethyl mercaptide, in as much as this reaction may be assumed to proceed with inversion of configuration[15] to give *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl thioether. This was also the product of the reduction of 4-*t*-butylcyclohexanone ethylene hemithioketal with mixed hydride (see below).

Several of the products were characterized by further chemical transformation. Thus β-hydroxyethyl cyclohexyl sulfide was transformed to β-chloroethyl cyclohexyl sulfide by treatment with hydrochloric acid or thionyl chloride (lower yield). The chloro compound, in turn, was reduced to cyclohexyl ethyl sulfide by means of lithium aluminum hydride. Analogously, *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl sulfide and iso(?)bornyl β-hydroxyethyl sulfide were converted to the corresponding β-chloroethyl sulfides and ethyl sulfides. *trans*-4-*t*-Butylcyclohexyl β-hydroxyethyl sulfide and the corresponding ethyl sulfide were also oxidized to the respective sulfones. *trans*-4-*t*-Butylcyclohexyl β-chloroethyl sulfide upon treatment with ethanolic sodium ethoxide gave the corresponding β-ethoxyethyl sulfide rather than a vinyl sulfide. These compounds are described in the Experimental part.

Stereochemistry and Mechanism of Hemithioketal Reduction.—Both epimers of 4-*t*-butylcyclohexanone ethylene hemithioketal upon treatment with "mixed hydride" gave the thermodynamically more stable *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl sulfide identical with the authentic sample mentioned earlier (Fig. 2). However, no conclusions can be drawn from this observation as to possible intermediates in the reduction, in as much as it was shown that the starting materials are interconverted under the conditions of the reaction. Somewhat more illuminating conclusions regarding reaction intermediates were drawn from a comparison of boron trifluoride with aluminum chloride as catalysts in the equilibration of I and II and in the reduction of I and II with combinations of these Lewis acids and lithium aluminum hydride. As was already mentioned, I and II are interconverted (equilibrated) by boron trifluoride. The reaction is clean; nothing besides equilibration happens even in a period of six months in anhydrous ether and the material put in is recovered, upon quenching with cold base, as either I or II. Lithium aluminum hydride in conjunction with BF_3 does *not* reduce I or II, although equilibration occurs in this case also. Aluminum chloride behaves differently. It also leads to equilibration of I and II, but the reaction is not clean; even after a few hours an insoluble precipitate appears and quenching with base at this stage produces considerable amounts of 4-*t*-butylcyclohexanone. On the other hand, aluminum chloride *does* promote reduction of 4-*t*-butylcyclohexanone ethylene hemithioketal with hydride. The most likely (although probably not unique) interpretation of these findings is shown in Fig. 3. Equilibration is assumed to proceed *via* a sulfocarbonium ion. This sulfocarbonium ion in itself is not reduced by hydride, however, for BF_3, which promotes equilibration, does not promote reduction. With aluminum chloride, on the other hand, further transformation of the sulfocarbonium ion to an α-halothioether occurs, in accordance with the more pronounced nucleophilic character of chloride compared to fluoride.[16] The α-chloroether may then be re-

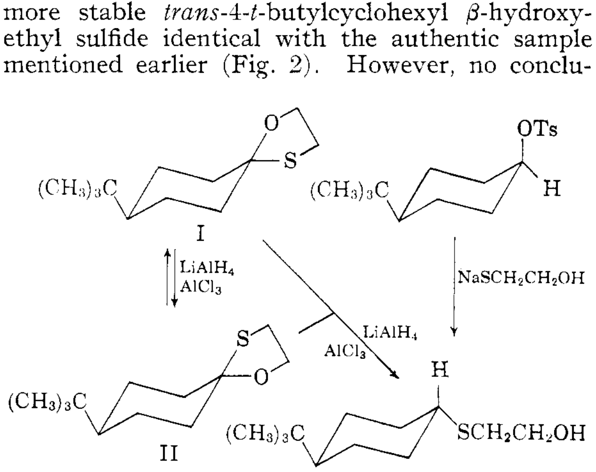

Fig. 2.—Reduction of 4-*t*-butylcyclohexanone ethylene hemithioketals with mixed hydride.

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[13] *Cf.* E. L. Eliel and L. A. Pilato, *Tetrahedron Letters*, 103 (1962). The conformational equilibrium constant for sulfur is calculated to be 0.4 kcal. mole from this observation.

[14] The isomer m.p. 112–113° is by far the minor constituent of the mixture of hemithioketals obtained by treating 3-cholestanone with mercaptoethanol. Treating this mixture with BF_3 is evidently a convenient means of enriching it with the lower-melting isomer. In contrast, treatment of 4-*t*-butylcyclohexanone with mercaptoethanol gave approximately the equilibrium mixture of the solid and liquid ketal. The difference may be merely one in reaction time: the 3-cholestanone derivative was prepared on a small scale in 6 hours, whereas reaction of the 4-*t*-butylcyclohexanone derivative (large batch) took 30 hours and may have entailed equilibration. In fact, previous investigators (refs. 7 and 10) may not have obtained the isomer m.p. 112–113° derived from cholestanone because they used even shorter reaction times. If this interpretation and our assignment of configuration are correct, the kinetically controlled product of the hemithioketalization is the epimer with equatorial sulfur, in accordance with the previous assumption (ref. 7b).

[15] *Cf.* E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1957).

[16] *Cf.* paper IX: M. N. Rerick and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2356 (1962).

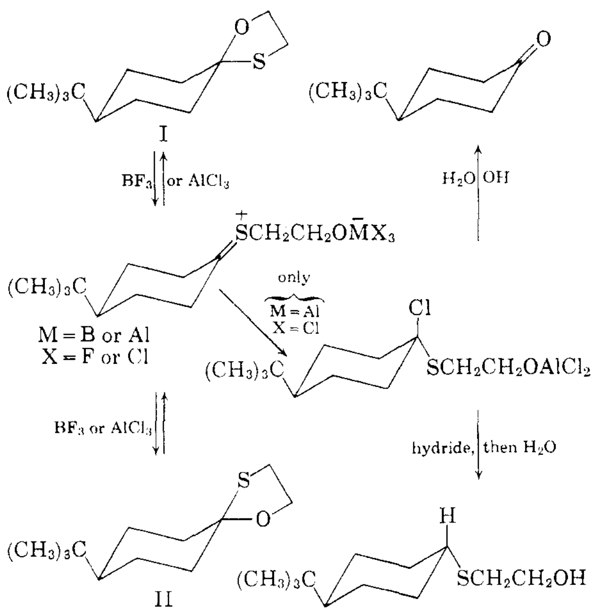
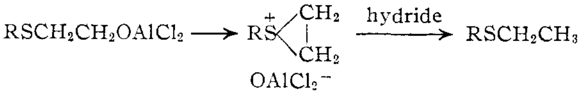


Fig. 3.—Mechanistic scheme for reduction and equilibration.

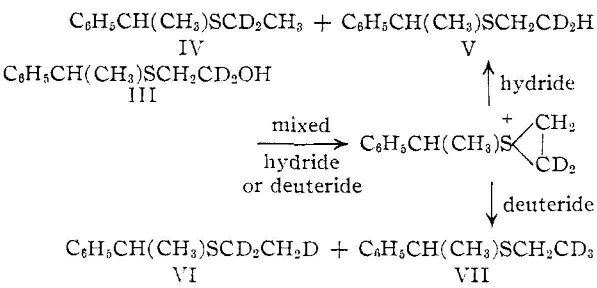
duced-phenyl chloromethyl sulfide, $C_6H_5SCH_2Cl$, was found in the present investigation to be readily reduced to thioanisole, $C_6H_5SCH_3$, with mixed hydride— or, if no reducing agent is present, it will be hydrolyzed to ketone upon quenching in base.[17] The salient feature of this mechanism is that the thiocarbonium ion cannot as such be reduced by hydride, but that storage in the form of an α-halothioether must precede reduction.[18]

Mechanism of Hydrogenolysis of β-Hydroxyethyl Thioethers.—Hydrogenolysis of alcohol and other functions by mixed hydride is a well-recognized reaction.[3] In general, only those functional groups are subject to hydrogenolysis which, upon departure, leave a stabilized carbonium ion. The very instances of reduction of hemithioketals, discussed in this paper, and of ketals, discussed in the previous one,[2] are cases in point: the first (although not necessarily the ultimate) intermediates are the relatively stable sulfocarbonium and oxocarbonium ions, respectively. Other well-studied cases concern the hydrogenolysis of benzyl and allyl alcohols[19,20] (involving the benzyl or allyl carbonium ion) and the hydrogenolysis of α-aminonitriles $RCH(NH_2)CN$ to amines[21] involving an iminocarbonium ion $RCH{=}NH_2^+$. In view of these analogies it appeared extremely likely that hydrogenolysis of β-hydroxyethyl thioethers would involve cyclic sulfonium ions (Fig. 4), since such sulfonium ions are well-recognized intermediates in the conversion of β-hydroxy sulfides to β-chloroethyl sulfides.[22] Proof of the correctness of this hypothesis was provided by a study of the hydrogenolysis of β,β-dideuterio-β-hydroxyethyl α-phenethyl sulfide (III) with lithium aluminum hydride–aluminum chloride and lithium aluminum deuteride–aluminum chloride, as shown in Fig. 5. The former reduction gave an approximately 50:50 mixture of the α,α-dideuterio- and β,β-dideuterioethyl sulfide (IV and V) whereas the latter gave equal amounts of the α,α,β-trideuterio- and β,β,β-trideuterioethyl sulfides (VI and VII). Analysis of the product mixtures in each case was effected very readily by nuclear magnetic resonance spectroscopy, since IV differs from V (and VI from VII) in gross and obvious ways, both as to the intensity of the signals produced by the ethyl groups and by their splitting. Quite accurate quantitative determinations of product composition could be effected by measurement of signal areas (see Experimental). The starting material III recovered from incomplete hydrogenolysis was unchanged in n.m.r. spectrum, indicating that no change in position of the tracer had occurred. Thus, in the hydrogenolysis, formation of the cyclic sulfonium ion is rate determining and is followed by a rapid hydrogenolysis which prevents return of the cyclic ion to starting material.



$$RSCH_2CH_2OAlCl_2 \longrightarrow \underset{OAlCl_2^-}{R\overset{+}{S}\langle{}^{CH_2}_{CH_2}} \xrightarrow{\text{hydride}} RSCH_2CH_3$$

Fig. 4.—Hydrogenolysis *via* sulfocarbonium ion.



$$C_6H_5CH(CH_3)SCD_2CH_3 + C_6H_5CH(CH_3)SCH_2CD_2H$$
IV V

$C_6H_5CH(CH_3)SCH_2CD_2OH$ III

$$\xrightarrow[\text{hydride or deuteride}]{\text{mixed}} C_6H_5CH(CH_3)\overset{+}{S}\langle{}^{CH_2}_{CD_2}$$

hydride; deuteride

$$C_6H_5CH(CH_3)SCD_2CH_2D + C_6H_5CH(CH_3)SCH_2CD_3$$
VI VII

Fig. 5.—Tracer study of cyclic sulfonium intermediate.

The method here described constitutes a facile and convenient synthesis of thioethers from carbonyl precursors and lends itself to "grafting" a thioethyl or β-hydroxythioethyl function on a variety of available carbonyl compounds. It is greatly preferable to the classical method of achieving the same objective—which would involve reduction of the carbonyl compound to an alcohol, conversion of the alcohol to the tosylate or halide and finally nucleophilic displacement (often in poor yield) by ethyl mercaptide or β-hydroxyethyl mercaptide.

Experimental

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Baird Associates instrument by Mr. Joel Livingston, Mr. Thomas Brett and Mr. Joseph West or on a Perkin-Elmer model 21 instrument by

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[17] H. Böhme, *Ber.*, **74**, 248 (1941).

[18] A comparable α-chloroether intermediate has been proposed in the reduction of mannitol 2,5-formal with boron trichloride followed by lithium aluminum hydride: T. G. Bonner and N. M. Saville, *J. Chem. Soc.*, 2851 (1960). We have found, however, (unpublished observation) that cyclohexanone ethylene ketal—in contrast to hemithioketals—may be hydrogenolyzed by lithium aluminum hydride in the presence of boron trifluoride; this hydrogenolysis probably does not involve an α-haloether (*cf.* A.-R. Abdum-Nur, and C. H. Issidorides, *J. Org. Chem.*, **27**, 67 (1962)). The mechanism of hydrogenolysis of ketals (as distinct from hemithioketals) thus appears as yet obscure.

[19] R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

[20] B. R. Brown and co-workers, *Chemistry & Industry*, 1307 (1956); *J. Chem. Soc.*, 2756 (1952); 3755 (1957); 1406 (1960).

[21] G. Le Ny and Z. Welvart, *Compt. rend.*, **245**, 434 (1957).

[22] R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946); R. C. Fuson and J. H. Koehneke, *ibid.*, **14**, 706 (1949).

L.A.P. Gas chromatograms were obtained on a Wilkens Instrument and Research model A-90-B aerograph. Nuclear magnetic resonance spectra were recorded with a Varian Associate high resolution instrument at 60 mc. by Mr. Bernard Nowak and Dr. Michael Gianni. Elementary analyses were performed by Midwest Microlab, Indianapolis, Ind.

Starting Materials.—The preparation[7] of the 4-*t*-butylcyclohexanone and 3-cholestanone ethylene hemithioketals and their equilibration is described in some detail. Other starting materials were prepared similarly and are listed in Table III.

4-*t*-Butylcyclohexanone (308 g., 2.0 moles) and 172 g. (2.2 moles) of β-mercaptoethanol were dissolved in 600 ml. of dry benzene containing a few crystals of *p*-toluenesulfonic acid. The solution was boiled under a reflux condenser equipped with a Dean and Stark trap until the theoretical amount of water (36 ml.) was collected; this took 30 hours. The solution was then cooled, extracted successively with 10% aqueous sodium hydroxide and three portions of water and then dried over potassium carbonate. Removal of the benzene by distillation left 400.0 g. (94%) of crude, semi-solid product whose infrared spectrum disclosed it to contain both epimeric hemithioketals as well as a small amount of unchanged ketone. (Further analysis was effected by chromatography of a small sample on alumina which indicated an approximate composition of 36% liquid hemithioketal, 60% of solid hemithioketal and 4% ketone.) As much of the solid isomer as possible was removed by filtration of the mush and further purified by chromatography of a hexane solution on alumina. The early fractions were discarded and the pure solid isomer was eluted with hexane–ether (9:1) and recrystallized from acetone–methanol; m.p. 74–75°. The infrared spectrum indicated absence of the stereoisomer as well as the starting ketone; the n.m.r. spectrum showed characteristic triplets at −175 c.p.s. (assigned to $\mathrm{SC}H_2$) and −245 c.p.s. (assigned to $\mathrm{OC}H_2$). (Shifts were measured in carbon tetrachloride solution with tetramethylsilane as standard using the audio oscillator side-band method.)

The filtrate from the solid isomer was distilled at reduced pressure and chromatographed in hexane on alumina. The early fractions (which were free of solid) were concentrated and distilled, b.p. 96–98° (0.2 mm.), n^{25}_{D} 1.5028. Low-temperature crystallization from ethanol gave material melting at 1–2°, whose infrared spectrum indicated absence of the solid epimer. The n.m.r. spectrum showed triplets at −177 c.p.s. ($\mathrm{SC}H_2$) and −243 c.p.s. ($\mathrm{OC}H_2$), and n.m.r. spectrum of a mixture of the two epimeric hemithioketals showed the expected doubling of both triplets, confirming that the observed differences in shift were real and not artifacts of the measurements.

3-Cholestanone (5.0 g., 0.013 mole) and β-mercaptoethanol (2.24 g., 0.029 mole) boiled in 100 ml. of benzene for 6 hours similarly gave 3.75 g. of crude product, m.p. 130–135° raised to 135–136°, $[\alpha]_D$ +23.6° ($CHCl_3$) (lit.[7] m.p. 135–136°, $[\alpha]^{20}_{D}$ +25°) upon recrystallization from acetone–methanol. On another occasion, this material was obtained with m.p. 144–145°. The two solids are apparently isomorphic, since they did not depress each other's melting point and recrystallization of the lower melting material using a seed crystal of the higher-melting raised the melting point to 138–140°. From the mother liquor of the above recrystallization was obtained 1.55 g. of material, m.p. 112–120°, which was chromatographed on basic alumina to give 0.5 g. of 3-cholestanone ethylene hemithioketal, m.p. 112–113°, $[\alpha]^{25}_{D}$ +31° ($CHCl_3$, *c* 3.05 g./100 ml.)

Equilibrations.—To a solution of 2.1 g. of 4-*t*-butylcyclohexanone ethylene hemithioketal, m.p. 1–2°, in 250 ml. of ether in a flask equipped with two reflux condensers and a sealed stirrer was added 3.38 g. of freshly distilled boron trifluoride etherate. The solution was boiled under an atmosphere of nitrogen with stirring for a total of 25 hours. The progress of the equilibration was followed by periodically quenching an aliquot of the solution in cold 10% sodium hydroxide (which was three times re-extracted with ether), drying the ether layer over potassium carbonate, concentrating and examining the infrared spectrum of the residue. A band at 10.45 μ, due to the solid epimer, at first grew and eventually became constant; at this point the infrared spectrum closely corresponded to that of a 50:50 mixture of the two isomers.

Similar equilibration of the isomer m.p. 74–75° gave a similar mixture after 24 hours. Column chromatography of an aliquot at this point yielded 211 mg. of liquid epimer, 244 mg. of solid isomer and 166 mg. of an approximately 50:50 (by infrared) intermediate fraction.

When 3.5 g. (0.0164 mole) of the solid isomer was treated with 0.46 g. (0.0033 mole) of boron trifluoride etherate in ether, equilibration proceeded very slowly. Solutions of the same proportions were therefore prepared from both the solid and the liquid epimers, and distributed over five or six ampoules each of which were flushed with dry nitrogen, and sealed. Periodic analysis indicated that it took *ca.* 6 months to reach equilibrium. After this time, the infrared spectra of the products from the epimeric starting materials had become identical. The residue from the liquid isomer was chromatographed giving 228.3 mg. of liquid isomer, 284.0 g. of solid isomer and 152.8 mg. of an intermediate fraction which was found by infrared spectrum to contain approximately 1 part of liquid isomer to 2 parts of solid. The over-all composition calculated from these data is 58% solid, 42% liquid. Similar analysis of the residue from the solid isomer indicated 57% solid, 43% liquid.

When equilibration was attempted with ethereal aluminum chloride, a precipitate appeared after a few hours. Work-up as above gave not only a mixture of hemithioketals but also large amounts of 4-*t*-butylcyclohexanone.

Equilibration of 1.9 g. of 3-cholestanone ethylene hemithioketal, m.p. 145°, with 11.25 g. of boron trifluoride etherate in ether gave, after a 5-hr. reflux, standing overnight and quenching as described, 1.9 g. of residue which, upon chromatography, was resolved into 0.57 g. of material, m.p. 144.5–146°; 0.31 g., m.p. 114–115°; and 0.77 g. of intermediate fraction which was rechromatographed. The second chromatogram returned 219 mg., m.p. 118–114°, and 442 mg., m.p. 112–120°. Assuming, thus, that the second fraction of the first chromatogram contained the solid and liquid isomer in a 1:2 ratio, it may be calculated that the original equilibrated mixture contained the two isomers in approximately equal proportions.

Reductions. (a) **Short Reaction Time.**—The reduction of acetophenone ethylene hemithioketal is described as typical. Other reductions were effected similarly. Yields of reduction products are listed in Table I and properties of products are listed in Table IV.

Aluminum chloride (8.33 g., 0.0625 mole) was placed in a 500-ml. three-necked flask equipped with a sealed stirrer, reflux condenser protected by a calcium chloride drying tube and pressure-equalized addition funnel. The flask was immersed in an ice-bath for approximately 1 hour and 100 ml. of cold ether (chilled an equal time in a closed flask in a deep-freeze chest at −8°) was added slowly with stirring. After all the aluminum chloride had dissolved, 16.4 ml. of 1.05 *M* ethereal lithium aluminum hydride (0.0156 mole) was added with continued cooling and stirring. After 15 min., 9.0 g. (0.05 mole) of acetophenone ethylene hemithioketal dissolved in 100 ml. of anhydrous ether was added slowly. Stirring was continued, but the ice-bath was removed and the solution heated at reflux for 2 hours. It was then cooled, 5–10 ml. of water was added to destroy the excess hydride and the solution was cleared by the addition of 100 ml. of 10% aqueous sulfuric acid. The ether layer was separated, the aqueous layer was extracted three times with 100-ml. portions of ether, and the combined ether layers were washed with water, dried over anhydrous magnesium sulfate and concentrated. Distillation of the residue gave 7.22 g. (78.5%) of β-hydroxyethyl α-phenethyl sulfide, b.p. 112° (0.55 mm.), n^{25}_{D} 1.5594, whose infrared spectrum was identical with that of a sample prepared from the sodium salt of β-mercaptoethanol and α-phenethyl chloride in 60% yield. The latter sample had b.p. 110° (0.5 mm.), n^{25}_{D} 1.5612.

(b) **Extended Reaction Time.**—The reduction of cyclohexanone ethylene hemithioketal is described as typical. Results of other reductions are listed in Table II and the products are included in Table IV.

Following the procedure described for acetophenone ethylene hemithioketal above, 8.0 g. (0.0505 mole) of cyclohexanone ethylene hemithioketal was reduced with 20 ml. of 1.26 *M* lithium aluminum hydride (0.025 mole) and 13.34 g. (0.1 mole) of aluminum chloride in ether solution. The solution was boiled at reflux for a total of 24 hours. The heterogeneous mixture was then worked up as described

TABLE III

STARTING MATERIALS

Ethylene ketal- or hemithioacetal of	Yield, %	M.p. or b.p., °C. (mm.)	n^{25}D	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Acetone	74	60 (67)	1.4724			[a]	
Heptaldehyde	71	76 (0.5)	1.4749	62.01	62.37	10.41	10.61
2-Octanone	80	120 (20)	1.4742	63.77	64.21	10.71	10.70
Cyclohexanone	92	106–107 (21)	1.5152			[b]	
4-Methylcyclohexanone[c]	75	104–106 (14)	1.5043	62.74	63.14	9.36	9.65
4-*t*-Butylcyclohexanone[d]	94	96–98 (0.2)	1.5028	67.23	67.41	10.35	10.33
		M.p. 74–75					
Camphor[e]	52	134–135 (16)	1.5228[f]	67.87	68.09	9.49	9.57
3-Cholestanone	65	M.p. 135–136[g] or 144–145		77.97	78.28	11.28	11.22[h]
		112–113			78.27		11.25
Benzaldehyde	80	98–100 (1.3)	1.5850			[i]	
Acetophenone	70	98 (1.3)	1.5640			[j]	
Trimethylene acetal or hemithioketal of							
Cyclohexanone	57	64–66 (0.3)	1.5128	62.74	62.64	9.36	9.05
Benzaldehyde	31	166 (1.2)	1.5795	66.62	67.14	6.71	7.16

[a] B.p. 70° (65 mm.), n^{24}D 1.4742 reported.[7a] [b] B.p. 47° (0.6 mm.), n^{24}D 1.5155 reported.[7a] [c] Product was a mixture of two epimers as indicated by n.m.r. [d] Two epimers formed, see text. [e] Diastereoisomeric nature of product unknown. [f] $[\alpha]^{25}$D +9.44° ($CHCl_3$, *c* 4.57 g./100 ml.). [g] M.p. 135–136° reported.[7a] [h] Calcd. S, 7.18. Found: S, 7.09%. [i] B.p. 86–87° (5 mm.) reported.[6] [j] B.p. 96° (2 mm.), n^{24}D 1.5663 reported.[7a]

TABLE IV

REDUCTION PRODUCTS

R in $RSCH_2CH_2OH$	M.p. or b.p., °C. (mm.)	n^{25}D	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
Isopropyl	90 (21)	1.4750			[a]	
n-Heptyl	105–106 (1.4)	1.4747			[b]	
2-Octyl	88 (0.3)	1.4737(20°)	63.10	63.02	11.65	11.66
Cyclohexyl	100 (1.0)	1.5122			[c]	
4-Methylcyclohexyl[d]	90–92 (0.15)	1.5025	62.01	61.80	10.41	10.19
trans-4-*t*-Butylcyclohexyl[e]	108–109 (0.4)	1.4938	66.61	66.83	11.18	11.58
Bornyl[f]	86–87 (0.02)	1.5195(20°)[g]	67.23	67.22	10.35	10.20
3-Cholestanyl[h]	M.p. 92–93		77.61	77.07	11.68	11.71
Benzyl	120 (1)	1.5726			[i]	
α-Phenethyl[j]	112 (0.55)	1.5594	65.89	65.78	7.74	7.66
R in $RSCH_2CH_2CH_2OH$						
Cyclohexyl[t]	108 (0.7)	1.5111	62.01	62.12	10.41	10.28
Benzyl	120 (0.4)	1.5642			[k]	
R in $RSCH_2CH_3$		n^{20}D				
n-Heptyl	96–97 (20)	1.4562			[l]	
2-Octyl	95 (10)	1.4558			[m]	
Cyclohexyl	70 (10)	1.4910			[n]	
trans-4-*t*-Butylcyclohexyl	80 (0.6)	1.4893			[o]	
Bornyl[p]	57–58 (0.05)	1.5035[q]	72.66	72.68	11.18	10.95
3-Cholestanyl[r]	M.p. 61–62		80.48	80.59	12.11	12.05
α-Phenethyl	60 (0.3)	1.5370				

[a] British Patent 733,123 ((1955), *C. A.*, **50**, 10799*f* (1956), reports b.p. 65–70° (17 mm.). An authentic sample prepared from isopropyl bromide and sodium β-hydroxyethylmercaptide was identical with the reduction product. [b] L. J. Goldsworthy, G. F. Harding, W. L. Norris, S. G. P. Plant and B. Selton, *J. Chem. Soc.*, 2177 (1948), report b.p. 153–154° (33 mm.). An authentic sample prepared from *n*-heptyl iodide and sodium β-hydroxyethyl mercaptide was identical with the reduction product. [c] M. Mousseron, R. Jacquier, M. Mousseron-Canet and R. Zagdoun, *Bul. soc. chim. France,* 1042 (1952), report b.p. 140° (18 mm.). An authentic sample prepared from cyclohexyl mercaptan and ethylene oxide was identical with the reduction product. [d] Stereochemistry unknown, probably *trans*. [e] An authentic sample prepared from *cis*-4-*t*-butylcyclohexyl tosylate and sodium β-hydroxyethylmercaptide was identical with the reduction product. [f] Stereochemistry unknown, may be isobornyl. [g] $[\alpha]^{25}$D −4.25° ($CHCl_3$, *c* 3.41 g./100 ml.). [h] Probably the β-isomer. [i] E. Fromm and H. Jörg, *Ber.*, **58B**, 304 (1925), report b.p. 169° (18 mm.). Identical with an authentic sample from sodium benzyl mercaptide and ethylene chlorohydrin. [j] An authentic sample prepared from sodium β-hydroxyethyl mercaptide and α-phenethyl chloride was identical with the reduction product. [k] S. Searles, *J. Am. Chem. Soc.*, **73**, 4515 (1951), reports b.p. 185° (22 mm.), n^{25}D 1.5632. An authentic sample prepared from benzyl mercaptan and 3-chloro-1-propanol was identical with the reduction product. [l] R. Adams, H. B. Bramlet and F. H. Tendick, *J. Am. Chem. Soc.*, **42**, 2369 (1920), report b.p. 190° (732 mm.), n^{20}D 1.4518. [m] Ref. 23 reports b.p. 87–89° (8 mm.), n^{20}D 1.4562. An authentic sample prepared from sodium ethylmercaptide and 2-octyl bromide was identical with the reduction product. [n] Ref. 23 reports b.p. 68–70° (10 mm.), n^{20}D 1.4908. An authentic sample prepared from sodium cyclohexyl mercaptide and ethyl bromide was identical with the reduction product. [o] Identical with sample described in text below. [p] Stereochemistry not proved, may be isobornyl. [q] $[\alpha]^{25}$D −4.1° ($CHCl_3$, *c* 6.56 g./100 ml.). [r] Probably β-isomer. [s] Ref. 23 reports b.p. 73–74° (3 mm.), n^{20}D 1.5397. An authentic sample prepared from sodium ethyl mercaptide and α-phenethyl chloride was identical with the reduction product. [t] An authentic sample prepared from cyclohexyl mercaptan and 3-chloro-1-propanol was identical with the reduction product (all identities were established by comparison of infrared spectra).

above and distilled to give 4.6 g. (63%) of ethyl cyclohexyl sulfide, b.p. 70° (10 mm.), $n^{20}D$ 1.4910 (lit.[23] b.p. 68–70° (10 mm.), $n^{20}D$ 1.4902), and 1.6 g. (20%) of β-hydroxyethyl cyclohexyl sulfide, b.p. 90° (0.8 mm.), $n^{20}D$ 1.5055. An authentic sample of ethyl cyclohexyl sulfide was prepared from sodium cyclohexylmercaptide and ethyl bromide in ethanol solution in 50% yield, b.p. 74–76° (10 mm.), $n^{20}D$ 1.4908; its infrared spectrum was identical with that of the above sample. The ether recovered in the concentration step was collected in two fractions. The second fraction contained a small amount of material which had the same retention time in a gas chromatogram as cyclohexene.

Attempted Reduction of 4-*t*-Butylcyclohexanone Hemithioketal (Liquid Isomer) with Lithium Aluminum Hydride–Boron Trifluoride.—To 7.35 ml. (0.058 mole, freshly distilled) boron trifluoride etherate was added 12 ml. (0.015 mole) of 1.26 *M* ethereal lithium aluminum hydride, followed by a solution of 6.2 g. (0.029 mole) of 4-*t*-butylcyclohexanone ethylene hemithioketal (isomer, m.p. 1–2°) in 100 ml. of anhydrous ether. The mixture was boiled for 2 hours and then poured into ice-cold 25% aqueous sodium hydroxide. The aqueous solution was extracted twice with ether and the combined ether layers were dried over potassium carbonate and concentrated. The residue (6.2 g.) was partly solid. Examination in the infrared showed only a very small hydroxyl band. Chromatography of the material on basic alumina yielded 3.7 g. of the liquid hemithioketal, identified by infrared spectrum and 2.2 g. of the solid. Less than 0.05 g. of *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl sulfide (identified by infrared spectrum) was recovered from the chromatogram.

Reduction of Phenyl Chloromethyl Sulfide with Mixed Hydride.—The mixed hydride solution was prepared from 13.33 g. (0.1 mole) of aluminum chloride in 100 ml. of ether and 30 ml. (0.025 mole) of 0.83 *M* ethereal lithium aluminum hydride. The phenyl chloromethyl sulfide (7.9 g., 0.05 mole) was added and the solution boiled at reflux for 6 hours. The usual work-up procedure (using 10% sodium hydroxide to solubilize aluminum salts) gave 4.1 g. (66%) of thioanisole, b.p. 83° (20 mm.), $n^{20}D$ 1.5865 (lit.[24] b.p. 187–190° (760 mm.), $n^{20}D$ 1.5869) identical in infrared spectrum with an authentic sample.

Cyclohexyl β-Chloroethyl Sulfide.—Forty milliliters of concentrated hydrochloric acid and 13.0 g. (0.0812 mole) of cyclohexyl β-hydroxyethyl sulfide were heated at reflux with stirring for 4 hours in a 500-ml. flask equipped with a reflux condenser protected by a trap and a sealed stirrer. Two additional portions of hydrochloric acid of 10 ml. each were added during this period. The mixture was cooled, allowed to stand overnight, poured into 100 ml. of water and extracted twice with 100-ml. portions of ether. The combined ether layers were washed with water and saturated sodium chloride solution, dried over magnesium sulfate and concentrated. Distillation of the residue gave 12.2 g. (84%) of cyclohexyl β-chloroethyl sulfide, b.p. 86–88° (0.4 mm.), $n^{25}D$ 1.5146. The same material was obtained, though only in 35% yield, by treating the β-hydroxyethyl sulfide with thionyl chloride in pyridine.

Anal. Calcd. for $C_8H_{15}ClS$: C, 53.76; H, 8.46. Found: C, 54.21; H, 8.48.

4-*t*-Butylcyclohexyl β-chloroethyl sulfide was prepared in the same way as the lower homolog, from 15.0 g. (0.07 mole) of 4-*t*-butylcyclohexyl β-hydroxyethyl sulfide and 100 ml. of concd. hydrochloric acid. The yield was 12.3 g. (76%), b.p. 98–100° (0.05 mm.), $n^{20}D$ 1.5060.

Anal. Calcd. for $C_{12}H_{23}ClS$: C, 61.37; H, 9.87. Found: C, 61.74; H, 9.76.

Bornyl or (Isobornyl) β-Chloroethyl Sulfide.—Similarly prepared from 4 g. (0.0187 mole) of bornyl (or isobornyl) β-hydroxyethyl sulfide and 50 ml. of hydrochloric acid, this material weighed 3.0 g. (69%) and boiled at 98° (0.2 mm.), $n^{20}D$ 1.5222, $[\alpha]^{25}D$ −3.4° ($CHCl_3$, *c* 7.40 g./100 ml.).

Anal. Calcd. for $C_{12}H_{21}ClS$: C, 61.90; H, 9.09. Found: C, 62.09; H, 9.14.

Cyclohexyl Ethyl Sulfide (By Reduction).—A solution of 1.062 g. (0.028 mole) of lithium aluminum hydride in 60 ml. of dry tetrahydrofuran was prepared in a 250-ml. three-necked round-bottom flask equipped with a reflux condenser protected by a calcium chloride drying tube, sealed stirrer and pressure-equalized addition funnel. Five grams (0.028 mole) of cyclohexyl β-chloroethyl sulfide in 30 ml. of tetrahydrofuran was added and the mixture was boiled with stirring for 18 hours. It was then cooled, excess hydride was destroyed by cold 10% sulfuric acid and the solution was extracted three times with 100-ml. portions of ether which were combined, washed with saturated sodium chloride solution, dried over potassium carbonate and concentrated. Distillation of the residue gave 2.6 g. (65%) of ethyl cyclohexyl sulfide, b.p. 72–74° (12 mm.), $n^{20}D$ 1.4890, identical with the authentic sample cited in Table IV, footnote *n*.

***trans*-4-*t*-Butylcyclohexyl Ethyl Sulfide.**—Similar reduction of 5.5 g. (0.023 mole) of *trans*-4-*t*-butylcyclohexyl β-chloroethyl sulfide with 0.88 g. (0.023 mole) of lithium aluminum hydride in a total of 200 ml. of THF gave 2.5 g. (55%) of *trans*-4-*t*-butylcyclohexyl ethyl sulfide, b.p. 124–126° (10 mm.), $n^{20}D$ 1.4879. This material was identical in infrared spectrum to that listed in Table IV.

Anal. Calcd. for $C_{12}H_{24}S$: C, 71.92; H, 12.07. Found: C, 72.07; H, 12.09.

Bornyl (or isobornyl) ethyl sulfide was prepared similarly from the chlorosulfide in 53% yield, b.p. 50° (0.06 mm.), $n^{20}D$ 1.5029, $[\alpha]^{25}D$ −4.1° ($CHCl_3$, *c* 6.56 g./100 ml.). This material was identical in infrared spectrum with the low-boiling fraction of the hydrogenolysis product of camphor ethylene hemithioketal (Table IV).

***trans*-4-*t*-Butylcyclohexyl β-Hydroxyethyl Sulfone.**—A solution of 0.6 g. (0.0028 mole) of *trans*-4-*t*-butylcyclohexyl β-hydroxyethyl sulfide in 1 ml. of glacial acetic acid and 2 ml. of 30% hydrogen peroxide was heated on a steam-bath for 15 min. and then poured on ice. The precipitate formed was collected, washed and dried; wt. 0.5 g. (73%), m.p. 109–112°. Recrystallizations from benzene–petroleum ether (b.p. 30–60°) raised the melting point to 112–113°.

Anal. Calcd. for $C_{12}H_{24}O_3S$: C, 58.03; H, 9.74. Found: C, 57.84; H, 9.67.

***trans*-4-*t*-butylcyclohexyl ethyl sulfone** was similarly prepared from the corresponding sulfide in 69% yield, m.p. 95–97°.

Anal. Calcd. for $C_{12}H_{24}O_2S$: C, 62.02; H, 10.41. Found: C, 62.31; H, 10.21.

***trans*-4-*t*-Butylcyclohexyl β-Ethoxyethyl Sulfide.**—Sodium ethoxide prepared from 0.5 g. (0.022 g.-atom) of sodium in 100 ml. of anhydrous ethanol and 4.0 g. (0.017 mole) of β-*trans*-4-*t*-butylcyclohexyl β-chloroethyl sulfide were boiled at reflux for 3 hours. Part of the ethanol was distilled and the residue diluted with water and extracted with three 100-ml. portions of petroleum ether (b.p. 30–60°) which were dried over potassium carbonate. Distillation yielded 3.3 g. (80%) of *trans*-4-*t*-butylcyclohexyl β-ethoxyethyl sulfide, b.p. 120° (0.8 mm.), $n^{20}D$ 1.4837, whose infrared and n.m.r. spectra were compatible with the assumed structure.

Anal. Calcd. for $C_{14}H_{28}OS$: C, 68.79; H, 11.54. Found: C, 68.50; H, 11.50.

4-Phenyl-3-thia-1,1-dideuteriopentanol, $C_6H_5CH(CH_3)SCH_2CD_2OH$.—α-Phenethylmercaptoacetic acid, $C_6H_5CH(CH_3)SCH_2CO_2H$, m.p. 61–63° (lit.[25] 61–63°), was prepared from phenylmethylcarbinol, mercaptoacetic acid and hydrochloric acid by the method of Holmberg.[25] Esterification of the acid with ethanol using sulfuric acid as a catalyst gave ethyl α-phenethylmercaptoacetate, b.p. 118–124° (0.3 mm.), $n^{20}D$ 1.5260, in 81% yield. Reduction of 11.0 g. (0.05 mole) of this ester with 1.26 g. (0.03 mole) of lithium aluminum deuteride in a total of 100 ml. of ether (6-hours reflux time) yielded 7.5 g. (82%) of 4-phenyl-3-thia-1,1-dideuteriopentanol, b.p. 112–114° (0.5 mm.), $n^{20}D$ 1.5618 (*cf.* data for corresponding unlabeled compound in Table IV).

Anal. Calcd. for $C_{10}H_{12}D_2OS$: C, 65.17; H, 7.66 (assuming H-D exchange in analyst's train[26]); D, 14.28. Found: C, 64.43; H, 7.80; D, 14.12.

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[23] W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

[24] K. Brand and K. W. Kranz, *J. prakt. Chem.*, [2] **115**, 143 (1927).

[25] B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 14 (1937); *C. A.*, **31**, 4292 (1937).

[26] *Cf.* E. L. Eliel, S. Meyerson, Z. Welvart and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960).

Analogous reduction of lithium aluminum hydride gave a product identical in infrared spectrum to that cited in Table IV, footnote *j*. The n.m.r. spectrum of this sample showed all the expected signals; phenyl, methine (quartet), methyl (doublet), SCH_2 (triplet), OCH_2 (triplet) and OH. The peak assigned to OCH_2 was missing in the n.m.r. spectrum of the deuterated material.

Reduction of 4-Phenyl-3-thia-1,1-dideuteriopentanol. (a) **With Lithium Aluminum Hydride–Aluminum Chloride.**—The hydride solution was prepared from 13.34 g. (0.1 mole) of aluminum chloride in ether and 20 ml. (0.025 mole) of 1.26 *M* ethereal lithium aluminum hydride. The alcohol (5.5 g., 0.03 mole) was added in ether solution and the reaction allowed to proceed for 19 hours at reflux with stirring. The usual work-up procedure yielded an oil which was purified by chromatography in hexane solution on basic alumina and then distilled; yield 2.35 g. (74% taking into account 2.0 g. of starting material recovered by ether elution of the chromatogram), b.p. 114–116° (20 mm.), $n^{20}\text{D}$ 1.5370 (*cf.* Table IV for the corresponding unlabeled material).

The infrared spectrum and n.m.r. spectrum of the recovered starting material were identical with the spectra of the material put into the reaction. The n.m.r. spectrum of the product was compared with that of unlabeled α-phenethyl ethyl thioether (Table IV, footnote *s;* the same material was obtained by treating α-phenethyl β-hydroxyethyl thioether with mixed hydride in the way described above for the deuterated compound). The unlabeled material showed signals for C_6H_5, CH_3–CH (doublet), C*H* (quartet) $\mathrm{C}\mathit{H}_2\mathrm{S}$ (quartet) and $\mathrm{CH_2C}\mathit{H}_3$ (triplet). In the spectrum of the deuterated product, the CH_2S peak was a doublet instead of a quartet and was also diminished in intensity relative to the other peaks. The CH_3 peak of the ethyl group was nearly a singlet (with perhaps small satellites on either side) and was also diminished in intensity. This is what one would predict for a mixture of $C_6H_5CH(CH_3)SCH_2CHD_2$ (A) and $C_6H_5CH(CH_3)SCD_2CH_3$ (B); the observations are incompatible with a product which is all A. Thus rearrangement of the ethyl group has taken place during reduction. From the relative areas of the methyl (0.32) and methylene signals (0.18) of the ethyl group, the ratio of A to B was 1:1 within the limit of experimental error.

(b) **With Lithium Aluminum Deuteride–Aluminum Chloride.**—This reduction was carried out in similar fashion, except that solid $LiAlD_4$ (1.05 g.) was used instead of hydride solution. The product boiled at 106–110° (12 mm.), $n^{20}\text{D}$ 1.5380. The n.m.r. spectrum in this case showed only singlets for both the methylene and the methyl groups of the ethyl thioether function and the ratio of the two signal areas (CH_3:CH_2 = 9.00:8.75) was within limits of experimental error of that expected for a 1:1 mixture of $C_6H_5CH(CH_3)SCD_2CH_2D$ and $C_6H_5CH(CH_3)SCH_2CD_3$.

Other Hydrogenolyses. (a) ***trans*-4-*t*-Butylcyclohexyl β-hydroxyethyl sulfide** (5.6 g., 0.026 mole) was treated with mixed hydride from 6.9 g. (0.052 mole) of aluminum chloride and 15.5 ml. (0.013 mole) of 0.83 *M* lithium aluminum hydride at reflux for 6 hours. There was obtained 1.4 g. (60.5% considering 2.5 g. of starting material recovered) of *trans*-4-*t*-butylcyclohexyl ethyl sulfide, b.p. 82° (0.25 mm.), $n^{20}\text{D}$ 1.4893 (*cf.* Table IV).

(b) **β-Hydroxyethyl Benzyl Sulfide.**—Using 20.5 g. (0.154 mole) of aluminum chloride and 28 ml. (0.0384 mole) of 1.4 *M* lithium aluminum hydride for 6.0 g. (0.0357 mole) of benzyl β-hydroxyethyl sulfide, very little reduction occurred even after 48 hours at reflux and 24 hours at room temperature. Only 0.7 g. of benzyl ethyl sulfide, b.p. 100° (10 mm.), $n^{20}\text{D}$ 1.5355 (lit.[27] b.p. 98–99° (13 mm.)) was isolated by chromatography on alumina, in addition to 4.7 g. of starting material.

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Mechanisms of Reactions of Sulfinic Acids. II. The Reaction of *p*-Tolyl Disulfide with *p*-Toluenesulfinic Acid

BY JOHN L. KICE[1] AND KERRY W. BOWERS

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A new oxidation–reduction reaction involving a sulfinic acid and a disulfide is described. The reaction, studied with *p*-toluenesulfinic acid and *p*-tolyl disulfide, has the stoichiometry shown in eq. 2. In acetic acid–1% H_2O containing reasonable amounts of sulfuric acid this reaction can be made to predominate over the normal disproportionation of sulfinic acids. Kinetic study of the reaction shows it to be first-order in sulfinic acid, with the rate strongly accelerated by increasing concentration of added strong acid and strongly retarded by increasing concentration of water. These facts, the somewhat unexpected dependence of the rate on disulfide concentration (eq. 4) and the catalysis of the reaction by added diphenyl sulfide, all seem most consistent with a mechanism involving equilibrium formation of the intermediate ion (I) (eq. 8 and 9) and its rate-determining decomposition, either by eq. 10, or by nucleophilic attack of disulfide (or sulfide) on this same ion, eq. 11. The thiolsulfonate is then presumably formed by the reactions 12, 13 and 15.

In the first paper of this series[2] the disproportionation of *p*-toluenesulfinic acid (eq. 1) was studied in acetic acid containing 0.5–5.0% water and 0.0–1.3 *M* sulfuric acid. The reaction was found to be second order in sulfinic acid, markedly

$$3\mathrm{ArSO_2H} \longrightarrow \mathrm{ArSO_2SAr} + \mathrm{ArSO_3H} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{Ar} = p\text{-}\mathrm{CH_3C_6H_4}\text{–}$$

retarded by added water, and only slightly accelerated by added strong acid. In the slower runs at 1 *M* H_2SO_4 we noticed the experimental second-order rate constant increased slightly toward the end of the run. Because of the large initial concentration of sulfuric acid and the relative insensitivity of the rate to strong acid, this was clearly not due to the small amount of sulfonic acid produced in the decomposition. Nor was it due to the thiolsulfonate produced, since a run with 0.03 *M* added thiolsulfonate showed no change in the initial second-order rate constant. However, it did show a more pronounced acceleration toward the end of the run. This led us to suspect that perhaps *p*-tolyl disulfide, a known hydrolysis product of *p*-tolyl *p*-toluenethiolsulfonate, accelerated the rate of disappearance of sulfinic acid. Since the extent of hydrolysis of the thiolsulfonate

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[1] To whom inquiries should be sent: Department of Chemistry, Oregon State University.

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