was added 1.8 g (0.026 mol) of sodium ethoxide in small portions over a period of 30 min. The resulting mixture was stirred for 2 days at room temperature, after which 14 ml of dilute hydrochloric acid was added. The ether layer was separated and washed with water, 5% sodium bicarbonate, water, and saline water and then dried over sodium sulfate. The solvent and excess ethyl α-bromopropionate were evaporated under reduced pressure. Tlc of the reaction mixture indicated the presence of the desired steroidal glycidic ester and three minor impurities. The mixture was chromatographed on 150 g of alumina (Woelm, neutral grade 2). Elution with petroleum ether (bp 30–60°) and benzene gave 5.05 g of **13** as a colorless semisolid which was homogeneous by tlc. Repeated efforts to obtain a satisfactory elemental analysis of this compound failed, apparently due to residual amounts of solvent present in the semisolid. However, mass spectral analysis gave a correct molecular ion peak of M^+ 486 for $C_{32}H_{54}O_3$, ir 1728 and 1755 cm^{-1} (carbonyl stretching of glycidic ester),[30] nmr 4.22 ppm (q, CH_2CH_3).

Sodium Glycidate of 5α-Cholestan-3-one (14).—To a solution of 957 mg (0.002 mol) of glycidic ester **13** in 5 ml of absolute ethanol was added 200 mg (0.003 mol) of sodium ethoxide and then 0.09 ml (0.005 mol) of water. The mixture was allowed to stand at room temperature for 30 min, during which time the sodium salt precipitated. An additional 5 ml of ethanol was then added and the mixture was refluxed for 1 hr. After cooling, 843 mg (88%) of pale yellow solid was collected by filtration. An analytical sample of **14** was obtained as a colorless solid after two recrystallizations from methanol.

Anal. Calcd for $C_{30}H_{49}O_3Na$: C, 74.95; H, 10.27. Found: C, 74.91; H, 10.08.

Anodic Reaction of the Sodium Glycidate of 5α-Cholestan-3-one (14).—A solution of 744 mg (1.5 mmol) of sodium glycidate **14** in 50 ml of methanol was electrolyzed (apparatus I) for 6 hr at 150 mA (14–17 V) with the solution temperature maintained at 14.5–16°. Work-up in the usual manner gave 668 mg of a neutral fraction, tlc of which showed the presence of two compounds, one of which absorbed short-wave uv light. The neutral products were chromatographed on two preparative tlc plates (silica gel, 1 mm thick) and developed continuously for 3 hr in hexane–ether (92:8). Elution of the uv absorbing zone from each plate gave a total of 207 mg (32%) of product. Approximately one-half of this was crystallized from methanol–acetone to give 73 mg of 3-acetyl-5α-cholest-2-ene (**15**) as clusters of colorless needles, mp 90–92°. The analytical sample had mp 92–92.5°, $[\alpha]^{20}D$ +91.2° ($CHCl_3$) [lit.[15] mp 90–91°, $[\alpha]^{15}D$ +93.8° ($CHCl_3$)]; ir 1670 ($CH_3C{=}O$) and 1642 cm^{-1} (>C=CH–); nmr 2.25 (s, $CH_3C{=}O$) and 6.80 ppm (m, >C=CH–).

Anal. Calcd for $C_{29}H_{48}O$: C, 84.40; H, 11.72. Found: C, 84.59; H, 11.96.

The material lacking uv absorption eluted from the plates (215 mg) was impure and was rechromatographed on a 1-mm preparative tlc plate, from which 106 mg of pure material was obtained. The solid was recrystallized from acetone to give 56 mg (11%) of 3ξ-acetyl-3ξ-methoxy-5α-cholestane (**16**) as colorless flakes: mp 100–101° (a second recrystallization from the same solvent raised this to 101–101.5°); $[\alpha]^{20}D$ +21.9° ($CHCl_3$); ir 1712 cm^{-1} ($CH_3C{=}O$); nmr 2.16 (s, $CH_3C{=}O$) and 3.12 ppm (s, $-OCH_3$).

Anal. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.07; H, 11.94.

Attempted Anodic Reaction of the Sodium Glycidate of Piperonal (17).—A solution of 714 mg of sodium glycidate **17**, prepared in the usual two-step synthesis, in 50 ml of methanol was electrolyzed with apparatus I for 6 hr in the usual manner. The solution turned red immediately at the outset of electrolysis and was deep purple after 10 min. Work-up of the reaction gave only 80 mg of a neutral fraction, which consisted of numerous products on the basis of tlc. The reaction was not further investigated.

Registry No.—**1**, 31045-09-7; **2**, 31045-10-0; **3**, 31107-22-9; **4**, 31045-11-1; **5**, 31045-12-2; **6**, 31045-13-3; **7**, 932-66-1; **7** semicarbazone, 7499-13-0; **8**, 15174-91-1; **10**, 31045-17-7; **11**, 31107-23-0; **11** semicarbazone, 31044-94-7; **12**, 31044-95-8; **12** oxime, 31044-91-4; **13**, 31107-17-2; **14**, 31044-92-5; **15**, 2310-32-9; **16**, 31045-21-3.

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Notes

Reductions of Thio Acids with Lithium Aluminum Hydride and Sodium Borohydride

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In a recent study on the reduction of certain organosulfur compounds,[1] it was reported that reduction of thiobenzoic acid with lithium aluminum hydride produced primarily benzyl mercaptan (90%) and a very small amount of benzyl alcohol. In contrast to this report, during a brief study of the reduction of thiobenzoic acid and thioheptanoic acid with lithium aluminum hydride, we observed that significant amounts of both alcohol and thiol were obtained. Therefore, we decided to make a systematic study of the reduction of thio acids, in order to determine how the relative amounts of sulfur and oxygen displacement (*i.e.*, alcohol and thiol formation, respectively) would be affected by the following factors: (1) nature of the group attached to the thiocarboxylate function, (2) type of metal hydride used, (3) method of reagent addition, and (4) presence of Lewis acid catalysts. The effect of the latter was of particular interest since it has been shown that lithium aluminum hydride reduction of thiol esters in the presence of boron fluoride[2] or aluminum chloride[3] occurs with oxygen displacement (thioether formation) as opposed to the sulfur displacement (alcohol and thiol formation) which occurs with lithium aluminum hydride alone. Similarly, hydrogenolysis of hemithioacetals and hemithioketals with lithium aluminum hydride–aluminum chloride results exclusively in cleavage of the carbon–oxygen bond.[4]

Results and Discussion

Table I shows the composition of the alcohol–thiol mixtures obtained by reduction of a series of thio acids

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(3) D. E. Bublitz, *ibid.*, **32**, 1630 (1967).

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TABLE I
COMPOSITION OF THIOL–ALCOHOL MIXTURES[a] FROM THE REDUCTION OF THIO ACIDS (RCOSH)

R	Registry no.	Reducing agent: $LiAlH_4$[b]	$LiAlH_4$–BF_3[c]	$NaBH_4$–$AlCl_3$
C_6H_5	98-91-9	56	70	86[d]
p-ClC_6H_4	31143-03-0	56	67	78
p-$MeOC_6H_4$	6279-44-3	53	76	95
n-C_5H_{11}	7530-91-8	45	60	
C_2H_5	1892-31-5	51		81

[a] Expressed as mole pecentage of thiol in the thiol–alcohol mixture. [b] Thio acid was added to the hydride. Inverse addition produced 45, 40, and 40% thiol from C_6H_5COSH, p-$MeOC_6H_4COSH$, and n-$C_5H_{11}COSH$, respectively. [c] Hydride was added to the mixtures of thio acid and boron fluoride etherate; $LiAlH_4$:BF_3:thio acid mole ratios, 1:0.8:0.8. [d] The mole percentage of thiol was 84 when $AlCl_3$ was omitted.

under a variety of conditions. Lithium aluminum hydride reduction occurs rapidly to give high yields (86–100%) of alcohol–thiol mixtures. As indicated in Table I, alcohol and thiol are formed in nearly equal amounts and the ratio is not significantly different for aliphatic, aromatic, and substituted aromatic acids. Also, the ratio was not affected by variation in the hydride concentration from 1 to 2 *M* or by changes in the $LiAlH_4$:thio acid mole ratio from 1.2 to 2.5. Slow, inverse addition of hydride results in a small but consistent increase in the proportion of alcohol formation over that observed when the thio acid was added to the hydride.

The data show that when boron fluoride etherate[5] and the thio acid are present in a 1:1 molar ratio, a significant increase in the proportion of oxide displacement (thiol formation) occurs. These reductions occurred rapidly and completely with yields in the range of 67–85%. A large excess (15:1) of boron fluoride etherate as described for the conversion of thiol esters to thioethers[2] reduced the total yield but did not result in further increase in the amount of benzyl mercaptan produced from thiobenzoic acid.

Sodium borohydride reduction of the thioacids in diglyme was investigated. Reduction of thiobenzoic acid with sodium borohydride alone was only about half complete after 2 days, but the sodium borohydride–aluminum chloride reagent described by Brown[6] caused essentially complete reduction in 0.5 hr with yields in the range of 78–95%. As seen in Table I, the proportion of oxygen displacement (thiol formation) is much higher than with the other reductants studied. In two cases investigated (thiobenzoic and thiopropanoic) the thio–alcohol ratio was nearly the same when $AlCl_3$ was omitted.

Experimental Section

Materials.—All compounds used in the study have been described previously. Authentic samples were either commercially available or prepared by standard procedures. Thiobenzoic acid was supplied by Evans Chemical Co.; the other thio acids were prepared from the corresponding acyl chlorides.[7] Equivalent weights of the thio acids were determined by iodine titration and found to be within at least 5% of the calculated values in all cases.

Methods of Analysis.—The mixtures of alcohols and thiols obtained by reduction of the thio acids were analyzed by vpc using an F & M Model 700 chromatograph. All analyses were done with a 4 ft × 0.25 in. aluminum column containing 15% Carbowax 20M on 60–80 mesh Chromosorb W (HMDS treated). Column temperatures were varied between 45 and 190° and flow rates from 60 to 120 ml/min so that short retention times were obtained (1.2–2.5 min for the alcohols). In all alcohol–thiol mixtures the thiol had the shorter retention time. Analysis was based on peak-height ratios. An average of six standard mixtures was prepared from the pure alcohol and thiol for each analysis. To assure accuracy of the peak-height analysis, slight adjustment of the flow rate was sometimes made, so as to reproduce identical retention times between runs. Yields were determined by addition of internal standards.

Lithium Aluminum Hydride Reductions.—In typical reductions 0.025 mol of the thio acid dissolved in 20 ml of ether was allowed to react with 0.031 mol of *ca.* 1 *M*, standardized $LiAlH_4$ solution. Solutions refluxed during addition and reaction was complete in less than 15 min. After hydrolysis with acid the ether solutions were analyzed directly by vpc. In a typical run using boron fluoride, 0.016 mol of *ca.* 1 *M* $LiAlH_4$ solution was added to a mixture of 0.0125 mol of the thio acid and 1.8 g (0.0125 mol) of redistilled boron fluoride etherate in 15 ml of ether.

Sodium Borohydride Reductions.—To 15 ml of a 1.04 *M* solution (0.016 mol) of $NaBH_4$ in diglyme, thio acid (0.0125 mol) in 5 ml of diglyme was added, followed by a solution of 0.005 mol of sublimed $AlCl_3$ in 5 ml of diglyme. The mixture was then stirred and heated at 75° for 30 min under nitrogen. The thiol–alcohol mixture was isolated by hydrolysis with acid and extraction with ether. The quantity of unreacted thio acid as determined by iodine titration after bicarbonate extraction of the ether solution was usually about 5%. In an experiment carried out under the same conditions but with the $AlCl_3$ omitted, 47% of thiobenzoic acid remained after 44 hr.

Registry No.—$LiAlH_4$, 16853-85-3; $NaBH_4$, 16940-66-2.

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(5) Aluminum chloride as catalyst under the same conditions gave 50% thiol from thiobenzoic acid and 51% thiol from thiohexanoic acid, in combined thiol–alcohol yields of 83 and 65%, respectively. Extensive side reactions evidently occur at other conditions (increase in $AlCl_3$:$LiAlH_4$ ratios up to 3.2; mode of reagent addition changed), so that yields as low as 50% from thiobenzoic acid and 30% from thiohexanoic acid were observed. However, the mole percentage of thiol produced did not vary extensively: for thiobenzoic acid 34–57% and thiohexanoic acid, 48–60%.

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Intramolecular Hydrogen Bonding in the 1,2-Diphenylethanol System

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The use of infrared spectroscopy to show the presence of intramolecular hydrogen bonding between hydroxyl groups and π electrons is well documented.[2] Of special interest is the work of Oki and Iwamura, who demonstrated, *via* ir, that benzyl alcohols undergo a type of intramolecular hydrogen bonding as in I.[3]

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