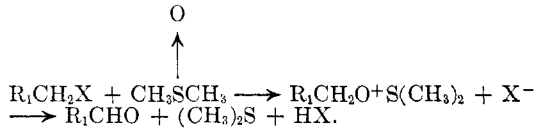
include dimethyl sulfide, methyl mercaptan and dimethyl disulfide. If an acid acceptor is not used, large amounts of formaldehyde are also formed. With diphenyl sulfoxide, a high-boiling residue, presumably diphenyl sulfide, is formed.

The formation of aldehyde can be conveniently accommodated by the following scheme:



$$R_1CH_2X + CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 \longrightarrow R_1CH_2O^+S(CH_3)_2 + X^-$$
$$\longrightarrow R_1CHO + (CH_3)_2S + HX.$$

$X = R_2SO_3^-$ or halogen.

Evidence for the existence of the intermediate salt has already been presented,[5] and Hunsberger and Tien have proposed a similar mechanism for ethyl bromoacetate with dimethyl sulfoxide.[4]

Complete details, including a study of reaction variables and experiments with other halides and sulfonates, will be reported later.

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meso- and *dl*-9,10-Octadecanediols[1]

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The 9,10-octadecanediols were desired as examples of secondary glycols. Stereochemically definitive syntheses of the *meso*- and *dl*-9,10-octadecanediols, by performic acid treatment of the corresponding *trans*- and *cis*-octadecenes, have been reported by Criegee and co-workers.[3]

Other workers[4,5] had reported the preparation of the "high-melting" forms of such glycols by catalytic hydrogenation of acyloins, but had experienced difficulty in isolating the "low-melting" forms in a pure state. Our own experience with platinum oxide hydrogenation of nonyloin was similar.

A more convenient method of preparation was found to be the reduction of nonyloin with sodium borohydride, which proceeded almost quantitatively to a mixture of the two forms. Separation by crystallization from aqueous ethanol gave yields of 42% of the *meso* and 56% of the *dl* modification. Identities were confirmed by independent preparation of the *meso* form by *cis*-hydroxylation[6] of *cis*-octadecene[7] with hydrogen peroxide–osmium tetroxide and of the *dl* form by ring opening, with Walden inversion,[8] performed on *cis*-9,10-epoxyoctadecane.[7]

Since greater solubility has been correlated with lower melting point and *dl* or *threo* configuration in the case of stilbene dibromide[9] and various esters of the isomeric 9,10-dihydroxystearic acids,[10,11] it was interesting to make solubility measurements (Table I) on the present diols and two related compounds.

TABLE I

SOLUBILITY OF 9,10-DISUBSTITUTED OCTADECANES, STEARIC ACIDS AND OCTADECANOLS

Compound	M.P.	Solvent	Solubility, g./l. of Soln. at 25°
meso-Octadecanediol	130°	95% EtOH	11.9
dl-Octadecanediol	78°	95% EtOH	30.2
meso-Octadecanediol	130°	Benzene	2.6
dl-Octadecanediol	78°	Benzene	13.7
erythro-Dihydroxystearic acid[a]	131°	95% EtOH	8.8
threo-Dihydroxystearic acid[a]	95°	95% EtOH	69.8
Dichlorooctadecanol[b]	31°	95% EtOH	19.0[d]
Dichlorooctadecanol[c]	12°	95% EtOH	843.[d]

[a] Ref. (8). [b] Presumably *erythro* since made by chlorination of elaidyl alcohol.[12] [c] Presumably *threo* since made by chlorination of oleyl alcohol.[12] [d] Measurements made at 0°.

In each case the *dl* or *threo* modification is considerably more soluble, as well as lower melting.

EXPERIMENTAL

meso-9,10-Octadecanediol by hydrogenation of nonyloin. Hydrogenation at room temperature of 10 g. of nonyloin over PtO_2, gave a 30% yield of 9,10-octadecanediol, m.p. 130.0–130.4° (reported[5] 127°,[3] 127.5–128°). On admixture this substance did not change the melting point of *meso*-9,10-octadecanediol reference compound. Its infrared spectrum measured on a KBr disk was superimposable on that of the reference compound.

meso- and dl-Octadecanediols by sodium borohydride reduction of nonyloin. In 235 ml. of 95% alcohol 18.7 g. of nonyloin was reduced by treatment with 1.24 g. of sodium boro-

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hydride. Crystallization from aqueous alcohol at room temperature gave 2.5 g. of *meso*-9,10-octadecanediol, m.p. 129.8–131.0° (reported[5] 127°,[3] 127.5–128°); on admixture it did not change the melting point of *meso*-9,10-octadecanediol reference compound. The infrared spectrum of this compound measured on a KBr disk was also superimposable upon that of the reference compound.

After the mother liquor had stood at 0°, a second crop of 5.4 g. of *meso*-9,10-octadecanediol was obtained of m.p. 129.2–131.0°. The total yield of the *meso*-diol was 7.9 g. (42%).

The filtrate from crop 2 on standing at −20° afforded 10.5 g. (56% yield) of *dl*-9,10-octadecanediol, m.p. 76.8–78.0° (reported[13] >70°,[3] 76–77°); on admixture with *dl*-9,10-octadecanediol reference compound the melting point was unchanged. The infrared spectra of this substance measured both on a KBr disk and on a CS_2 solution were superimposable on those of the reference compound.

meso-9,10-Octadecanediol, reference compound. Following the procedure of Woodward *et al*,[6] 1.2 g. of *cis*-9-octadecene[7] was *cis*-hydroxylated by treatment in ether solution for 48 hr. with hydrogen peroxide and a little osmium tetroxide. Crystallization at −20° yielded 0.541 g. of the impure product and, after recrystallization from 95% ethyl alcohol and from ligroin at −20°, 0.185 g. of *meso*-9,10-octadecanediol, m.p. 127.4–129.0° (reported[5] 127°,[3] 127.5–128°).

dl-9,10-Octadecanediol, reference compound. Following the procedure of Swern,[8] 1.07 g. of *cis*-9,10-epoxyoctadecane,[7] heated 1 hr. at 100° in 25 ml. of anhydrous formic acid, yielded after saponification and two recrystallizations at −20° from ethanol 0.35 g. of *dl*-9,10-octadecanediol, m.p. 75.8–77.6° (reported[13] >70°,[3] 76–77°).

Solubility determinations. Twenty-five ml. portions of saturated solutions of the 9,10-octadecanediols, dihydroxystearic acids, and dichlorooctadecanols were freed of solvent by evaporation under an air jet and heating for 1.5 hr. at 50° and 1 mm. pressure. The weights of the residues permitted calculation of the solubilities reported in Table I.

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Preparation of *O*-Phenyl-DL-homoserine and of DL-Homoserine from α-Phthalimido-γ-butyrolactone

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In previous studies[1,2,3] it was shown, that α-amino-γ-butyrolactone, in its free and masked forms, can be converted into the corresponding γ-substituted α-amino acids.

As polymerization of *O*-phenyl-DL-homoserine resulted in high molecular, fiber-forming polypeptides,[4] it was of interest to obtain the starting material by a simpler method than hitherto[5] known. The easy availability of α-phthalimido-γ-butyrolactone[3] renders this compound a useful intermediate in the synthesis of *O*-phenyl-DL-homoserine. As direct opening of α-phthalimido-γ-butyrolactone proved successful, the following procedure has been worked out: by reaction of α-phthalimido-γ-butyrolactone with sodium phenoxide α-phthalimido-γ-phenoxybutyric acid (I) was prepared. Removal of the phthaloyl group was carried out by hydrolysis with 18% hydrochloric acid and α-amino-γ-phenoxybutyric acid hydrochloride isolated, from which the free *O*-phenyl-DL-homoserine (II) was obtained by treatment with triethylamine. Overall yield based on α-phthalimido-γ-butyrolactone was 42–45%, on γ-butyrolactone 27–29%.

Previously[2] we have described the synthesis of α-amino-γ-iodobutyric acid hydroiodide from α-bromo-γ-butyrolactone and aqueous ammonia. Some difficulties are encountered in the removal of the admixed salts from the intermediate α-amino-γ-butyrolactone hydroiodide. These are avoided in the present synthesis by employing α-phthalimido-γ-butyrolactone, which reacts with 55% hydroiodic acid, yielding α-amino-γ-iodobutyric acid hydroiodide (III) without any opportunity of its contamination by inorganic salts. From α-benzamido-γ-butyrolactone,[1] the hydroiodide (III) was prepared in a similar manner.

Hydrolysis of α-phthalimido-γ-butyrolactone with 24% hydrobromic acid gave α-amino-γ-butyrolactone hydrobromide (IV), as expected,[2] without opening of the lactone ring.

The convenient preparation of α-phthalimido-γ-butyrolactone and its ready hydrolysis by sulphuric acid renders this compound also an advantageous intermediate for a smooth synthesis of DL-homoserine. Overall yield was 50–55% of recrystallized homoserine based on γ-butyrolactone.

EXPERIMENTAL

α-Phthalimido-γ-phenoxybutyric acid (I). Clean sodium (4.6 g., 0.2 mole) was cautiously added in portions, and with occasional shaking, to an excess of molten phenol, placed in a flask fitted with an air condenser and a drying tube containing calcium chloride, the rate of addition being sufficient to keep the phenol molten. The mixture was finally heated until the sodium was dissolved, then gently refluxed for 5 min., and allowed to cool. After addition of α-phthalimido-γ-butyrolactone[3] (46 g., 0.2 mole), heating to reflux for 1/2 hr., and subsequent cooling, the solidified mixture was triturated with 250–300 ml. of ether, and the crude sodium

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