

meso- and dl-9,10-Octadecanediols¹A. N. WRIGLEY, F. D. SMITH, AND A. J. STIRTON²

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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*-hydroxylation⁶ of *cis*-octadecene⁷ with hydrogen peroxide-osmium tetroxide and of the *dl* form by ring opening, with Walden inversion,⁸ performed on *cis*-9,10-epoxy-octadecane.⁷

Since greater solubility has been correlated

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with lower melting point and *dl* or *threo* configuration in the case of stilbene dibromide⁹ 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°
<i>meso</i> -Octadecanediol	130°	95% EtOH	11.9
<i>dl</i> -Octadecanediol	78°	95% EtOH	30.2
<i>meso</i> -Octadecanediol	130°	Benzene	2.6
<i>dl</i> -Octadecanediol	78°	Benzene	13.7
<i>erythro</i> -Dihydroxystearic acid ^a	131°	95% EtOH	8.8
<i>threo</i> -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 PtO₂ gave a 30% yield of 9,10-octadecanediol, m.p. 130.0–130.4° (reported⁶ 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° (reported⁵ 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° (reported¹³ >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 CS₂ 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-octadecene⁷ 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° (reported⁵ 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° (reported¹³ >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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