[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. II. The Composition of Dipropenyl Glycol[1]

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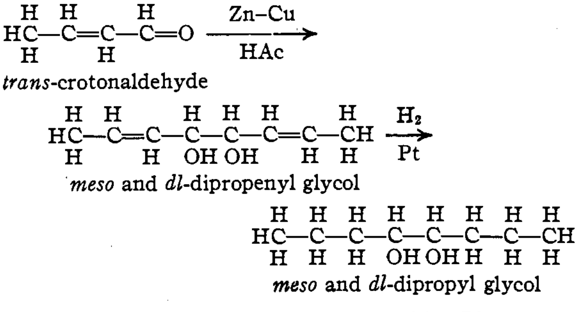
In continuing the study of methods of synthesis of pure isomers of the aliphatic polyene hydrocarbons of known configuration[2] it was important to know the composition of dipropenyl glycol. Since Kuhn and Rebel[3] reported that only one of the expected isomeric glycols was formed during the pinacolic reduction of aldehydes, we would expect that the reduction of *trans*-crotonaldehyde would produce only *dl, trans-trans*-dipropenyl glycol. However, if this were the case it would be difficult to explain the formation of two tetrabromides[4] or of two dimethylhexatrienes[5] from dipropenyl glycol. Since Kuhn and Rebel's method of oxidizing the dipropenyl glycol to racemic tartaric acid (by several steps) resulted in poor yields, they were not justified in concluding that only one stereoisomeric form was present in the original glycol. Accordingly, we reinvestigated the composition of dipropenyl glycol prepared by the pinacolic reduction of crotonaldehyde and reported[6] the formation and isolation of both *meso* and *dl*-dipropyl glycols from the catalytic reduction of dipropenyl glycol. The reactions involved were as follows



$$\underset{H}{\overset{H}{HC}}-\overset{H}{C}=\underset{H}{C}-\overset{H}{C}=O \xrightarrow[HAc]{Zn-Cu}$$

trans-crotonaldehyde

$$\underset{H}{\overset{H}{HC}}-\overset{H}{C}=\underset{H}{C}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{C}=\overset{H}{\underset{H}{C}}-CH \xrightarrow[Pt]{H_2}$$

meso and *dl*-dipropenyl glycol

$$\underset{H}{\overset{H}{HC}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{CH}$$

meso and *dl*-dipropyl glycol

Contrary to the opinion expressed by Kuhn and Rebel,[3] several other investigators have clearly demonstrated that both *meso* and *dl* forms are produced by the pinacolic reduction of aldehydes. The duality of divinyl glycol has been established by separation into the *meso* and *dl* forms,[7] by hydrogenation to *meso* and *dl*-diethyl glycols[8] and by conversion into *dl*-mannitol[9] and allodulcitol.[10] The duality of dipropenyl glycol has also been conclusively established since our oral report[6] was made. Wiemann[11] treated the glycol with phenyl isocyanate and isolated a solid phenylurethan from which he recovered on hydrolysis *meso*-dipropenyl glycol, m. p. 48°. By catalytic reduction[12] of his dipropenyl glycol he obtained both the solid *meso*- and the liquid *dl*-dipropyl glycols which had been prepared from butyroin by Bouveault and Locquin[13] and identified by Veibel.[14]

Although the above-mentioned workers have established the fact that the pinacolic reduction of aldehydes gives both *meso*- and *dl*-glycols, they have not answered the important question which originally prompted the work on this subject. Kuhn and Rebel[3] had suggested that, from purely geometrical grounds, in such reactions there should be formed 25% each of the *d*- and *l*- and 50% of the *meso*-glycol. It is the purpose of this paper to show that in the case of the pinacolic reduction of crotonaldehyde, at least, the *meso*- and *dl*-glycols actually are formed in equal quan-

TABLE I

MELTING POINTS OF BI-3,5-DINITROBENZOATES FROM KNOWN MIXTURES OF DIPROPYL GLYCOLS

% *meso*-dipropyl glycol	M. p., °C. of dinitrobenzoate
0	125 –125.3
3	124.3–126.5
5	124.8–131
7	124.1–135
10	124.2–143
50	123.7–182
100	200.3–200.4
Eutectic	124 –128
Original mixture	123 –181

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[1] This work was started in 1930 by the senior author during the tenure of a National Research Council Fellowship at Stanford University. The authors are indebted to Colorado College for the use of library and stenographic facilities during the preparation of this manuscript.

[2] Young, THIS JOURNAL, **54**, 2498 (1932).

[3] Kuhn and Rebel, *Ber.*, **60B**, 1565 (1927).

[4] Charon, *Ann. chim. phys.*, [7] **17**, 260 (1899).

[5] Urion, *Compt. rend.*, **196**, 353 (1933); *Ann. chim.*, [11] **1**, 5 (1934).

[6] A preliminary report of this work was presented before the Organic Division at the Denver meeting of the American Chemical Society, August, 1932.

[7] Van Romberg and Van Hasselt, *Proc. Acad. Sci. Amsterdam*, **35**, 40 (1932).

[8] Farmer, Laroia, Swift and Thorpe, *J. Chem. Soc.*, 2937 (1927).

[9] Lespieau and Wiemann, *Compt. rend.*, **194**, 1946 (1932).

[10] Lespieau and Wiemann, *ibid.*, **195**, 886 (1932).

[11] Wiemann, *ibid.*, **197**, 1654 (1933).

[12] Wiemann, *ibid.*, **196**, 118 (1933).

[13] Bouveault and Locquin, *ibid.*, **140**, 1699 (1905).

[14] Veibel, *Biochem. Z.*, **239**, 456 (1931).

tities. This has been accomplished by determining the phase relationships existing between the *meso-* and *dl*-dipropyl glycols (Fig. 1) prepared from the dipropenyl glycol and by comparing the melting points of the bi-3,5-dinitrobenzoates prepared from the pure *meso-* and *dl*-dipropyl glycols and from various mixtures of these glycols (Table I). In this work the *dl*-dipropyl glycol, m. p. 28°, was obtained in a pure form for the first time.

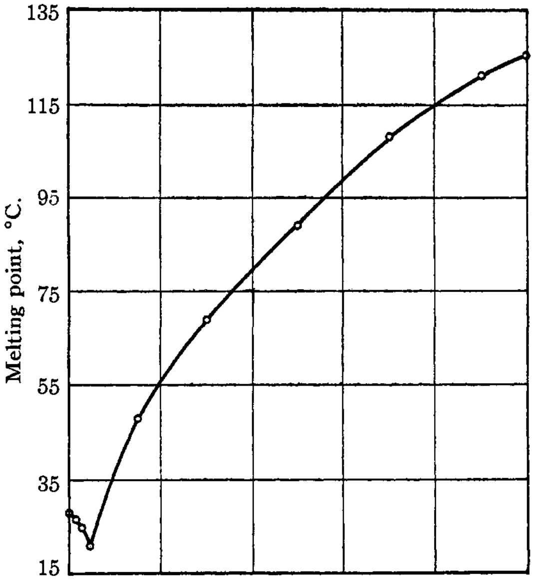
Experimental Part

The Preparation of Dipropenyl Glycol.—Several kilograms of dipropenyl glycol were prepared by the reduction of 200-g. portions of *trans*-crotonaldehyde[2] in a dilute solution of acetic acid according to Charon's method.[4] Special care was exercised to prepare an active zinc–copper couple[15] and to keep the temperature of the reaction mixture between −5 and −10° during the reduction. After the reaction mixture was filtered to remove the zinc–copper residue, it was extracted 7–8 times with 250-ml. portions of ether to assure the removal of the constituents which absorb bromine. It was also advantageous to neutralize the ether extract with potassium carbonate before removing the solvent. A fractional distillation of the product through a 90-cm. Claisen-head column filled with glass rings and equipped with a Hopkins condenser gave the two main fractions: crotyl alcohol, b. p. 117–120° (15% of theoretical), and dipropenyl glycol b. p. (9 mm.) 113.4–114.4° (67%). These yields are similar to those reported by Charon[4] but contrary to those reported by Kuhn and Rebel.[3]

Fractional Distillation of Dipropenyl Glycol.—Several distillations of dipropenyl glycol, b. p. (9 mm.) 113.4–114.4°, d^{20}_4 0.9744, through the fractionating column described above, failed to produce any evidence of separation into *meso-* and *dl*-isomers. The failure to separate the isomers by distillation is not surprising, since Van Romberg and Van Hasselt[7] have shown that in the case of the closely related *meso-* and *dl*-divinyl glycols the isomers possess the same boiling point.

Catalytic Hydrogenation of Dipropenyl Glycol and the Isolation of *meso-* and *dl*-Dipropyl Glycols.—Freshly distilled dipropenyl glycol (72 g.) was reduced with the aid of a platinum catalyst[16] in 200 ml. of 95% ethanol. The solvent was removed through a Hempel column and the mushy residue, m. p. 20–90°, was filtered. The solid portion after recrystallization from petroleum ether was found to be *meso*-dipropyl glycol, m. p. 123.5–124.5°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.69; H, 12.42. Found: C, 65.67; H, 12.41.



Mole per cent. of *meso*-dipropyl glycol.

Fig. 1.—The melting point diagram of the system *meso*-*dl*-dipropyl glycols.

The filtrate was then fractionally distilled several times through the column described above. A fraction (1), b. p. (9.5 mm.) 110–111°, was obtained which was thought to be the pure *dl*-isomer. When a cooling curve was made the liquid supercooled easily due to its high viscosity but when seeded it solidified at 20.0–20.5°. The temperature remained constant for several hours when the bath temperature was held slightly above or below 20°, the only difference being in the quantity of crystals present in the mixture. However, when some of this fraction was converted into the bi-3,5-dinitrobenzoate, the product melted over a range indicating that the glycol fraction might not be a pure product, as suggested by the melting point. Consequently, a cooling curve was made using another fraction (3) which had some solid *meso*-glycol present even at 43°. As the mixture was cooled the quantity of solid increased until the temperature reached 15°. At this point a sudden evolution of heat occurred, the temperature rose to 20.0–20.5°, and the mixture solidified completely. The most likely explanation of this result is that 20.0–20.5° is the eutectic temperature for the system *dl-* and *meso*-dipropyl glycol. The *dl*-component failed to form when the eutectic temperature was reached, causing a metastable condition to exist, but as soon as some of the *dl*-component was formed an equilibrium was established immediately at the eutectic temperature. Fraction 1 was therefore subjected to several more fractional distillations until the main fraction had the same melting point after two consecutive distillations. This fraction was *dl*-dipropyl glycol, b. p. (9 mm.) 109.8–110°, m. p. 28°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.67; H, 12.42. Found: C, 65.59; H, 12.43; $n^{24.5}_D$ 1.4419.

In a series of experiments the yield of *meso*-glycol was approximately 95% of that expected if the dipropenyl glycol contained equal quantities of *meso-* and *dl*-forms. The

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(15) The zinc–copper couple was prepared by the method of Gladstone and Tribe, *J. Chem. Soc.*, **31**, 561 (1877), except that the copper sulfate solution was added to 80-mesh zinc in smaller portions and the reaction mixture was allowed to become decolorized completely before another portion was added. Although the yields of glycol decreased 10–15% if the sulfate solution were added in too large portions, nevertheless, we never obtained yields as low as those reported by Kuhn and Rebel.[3]

(16) Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York City, Vol. VIII, 1928, p. 92.

yield of *dl*-isomer was about 10% lower than the *meso*-form due to unavoidable losses during the many fractionations.

Analysis of Mixtures of the Dipropyl Glycols by Conversion into 3,5-Dinitrobenzoates.—In order to follow the degree of separation of the dipropyl glycols during the fractional distillation of large batches of material, it was desirable to have a convenient method of analysis. The preparation of the bi-3,5-dinitrobenzoates proved satisfactory for this purpose. It was found that 3,5-dinitrobenzoic acid, its acid chloride and the mono-ester of the glycols were all fairly soluble in a mixture of alcohol and nitrobenzene, while the di-esters of both glycols were insoluble. It was therefore possible to recrystallize the di-esters made from glycol mixtures without changing their composition. The crude esters were prepared from 0.3 g. of the glycol, 6 ml. of dry pyridine, and 1.2 g. of 3,5-dinitrobenzoyl chloride in the usual manner. The crude product thus obtained was dissolved in 4–5 ml. of warm nitrobenzene and then 40–50 ml. of alcohol was very slowly added to ensure the formation of crystals instead of oil. The product was finally filtered, washed with cold alcohol and dried in a vacuum desiccator; yield, 90–95% of theoretical based on the di-ester. Bi-3,5-dinitrobenzoate from *meso*-dipropyl glycol, m. p. 200.3–200.4°.

Anal. Calcd. for $C_{22}H_{22}O_{12}N_4$: C, 49.42; H, 4.15; N, 10.49; mol. wt., 530. Found: C, 49.40; H, 4.10; N, 10.69; mol. wt., 540 (in nitrobenzene). Bi-3,5-dinitrobenzoate from *dl*-dipropyl glycol, m. p. 125–125.3°. *Anal.* Found: C, 49.58; H, 4.21; N, 10.59; mol. wt. 538 (in nitrobenzene). The melting points of esters made from known mixtures and from the original mixture of dipropyl glycols are given in Table I. It will be seen that the eutectic mixture contains about 4.5% *meso*-glycol and the original mixture 50% *meso*-glycol.

The Melting Point Diagram for the System *meso-dl*-Dipropyl Glycol.—In view of the fact that distillation methods did not give a satisfactory estimate of the composition of the dipropyl glycol mixture obtained from the catalytic reduction of dipropenyl glycol, it was necessary to construct a melting point diagram for the system *meso-dl*-dipropyl glycol. The eutectic temperature for mixtures of *meso* and *dl*-dipropyl glycols was determined by the Beckmann method on ten different mixtures of glycols. The average value for these runs was 20.7 ± 0.5°. Due to the extreme viscosity of the glycol mixtures and since the Beckmann method is subject to more or less error,[17] the remaining data were obtained by the melting point method. Known mixtures of *dl*- and *meso*-dipropyl glycols were sealed in small tubes which were heated slowly in a water-bath under constant agitation. The temperature at which the last particle of solid disappeared was recorded as the melting point. The temperature of the bath was raised slowly (never faster than 1° in five to ten minutes) and all melting points were duplicated with at least two different tubes. In all mixtures richer in *meso* than the eutectic, the solid phase in equilibrium with the liquid was found to be the *meso*-isomer. The results are recorded in Fig. 1. The composition of the eutectic mixture was found to be about 5% *meso*- and 95% *dl*-dipropyl glycol. The composition of the crude glycol mixture obtained from the reduction of dipropenyl glycol proved to be 50% *meso* and 50% *dl* since the final melting point of this mixture was 90°. It may therefore be concluded that the pinacolic reduction of crotonaldehyde gives equal quantities of *meso*- and *dl*-dipropenyl glycol.

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Summary

Dipropenyl glycol obtained from the pinacolic reduction of crotonaldehyde has been found to contain equal quantities of the *meso*- and *dl*-glycols.

Pure *dl*-dipropyl glycol and the bi-3,5-dinitrobenzoates of both *meso*- and *dl*-dipropyl glycols have been prepared for the first time.

The melting point diagram of the system *meso*-*dl*-dipropyl glycol is given.

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[17] Skau and Rowe, THIS JOURNAL, **57**, 2437 (1935).