mostly to β-olefins.[6] Hence, the following reaction seems to take place during the decomposition process

$$C_6H_{12}\ (\text{Hexene-1}) \longrightarrow C_6H_{12}\ (\text{Hexene-2}) \qquad (4)$$

The formation of hexene-3 is also possible, but less likely.

The readings of refractive index of the products also check with the above assumption. A mixture of 70% of *n*-hexane and 30% of hexene-2 (or hexene-3) would have $n^{20}\text{D}$ about 1.382, while the value of the portion boiling between 66–70° before sulfuric acid treatment was 1.384. A mixture of hexene-1, which possesses a much lower $n^{20}\text{D}$, and *n*-hexane would give a far smaller value.[2]

The elucidation of the exact mechanism of the decomposition process requires further study. Owing to the present wartime pressure and difficulties, the investigation on this subject had to be discontinued.

(6) Brooks and Humphrey, THIS JOURNAL, **40**, 832 (1918).

THE RESEARCH LABORATORIES
THE TUNG LI OIL WORKS
CHUNGKING, CHINA

RECEIVED JANUARY 2, 1943

Investigations on the Stereoisomerism of Unsaturated Compounds. VI. The Composition of Divinyl Glycol from Acrolein. The System *meso-dl*-Diethyl Glycol

BY WILLIAM G. YOUNG, STANLEY J. CRISTOL AND FRED T. WEISS

It has been demonstrated conclusively that diastereomeric unsaturated glycols are formed in the pinacolic reduction of α,β-unsaturated aldehydes.[1,2,3,4] Young, Levanas and Jasaitis[3] have shown that, in the reduction of crotonaldehyde, *meso*- and *dl*-dipropenyl glycols, which may be hydrogenated to the corresponding dipropyl glycols, are formed in equal amounts as predicted on purely geometric grounds, but not found, by Kuhn and Rebel.[5] van Risseghem has prepared the diastereomeric diethyl glycols from acrolein by the similar reaction path

$$CH_2{=}CHCHO \xrightarrow[\text{HOAc}]{\text{Zn-Cu}}$$

$$CH_2{=}CHCHOHCHOHCH{=}CH_2 \xrightarrow{H_2(Pt)}$$

meso- and *dl*-divinyl glycol

$$CH_3CH_2CHOHCHOHCH_2CH_3$$

meso- and *dl*-diethyl glycol

and has identified the individual isomers.

In the course of a study on the preparation of a number of pure stereoisomeric dibromides, we have prepared and separated the *dl*- and *meso*-diethyl glycols and have shown that the divinyl glycols are formed in equal quantities during the reduction of acrolein alone or in a mixture of acrolein and crotonaldehyde, contrary to the observations of Kuhn and Rebel.[5] This was accomplished by a determination of the melting point–composition diagram (Fig. 1) obtained by mixing the pure diastereomers, and by the use of this curve in a comparison with the melting point of the product mixture.

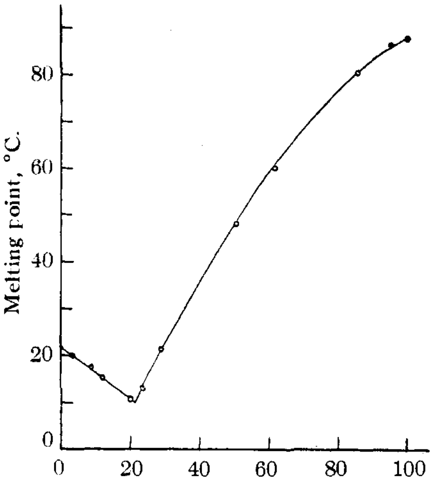

Fig. 1.—The melting point diagram of the system *meso*-, *dl*-diethyl glycol.

Experimental

Preparation and Separation of the Diethyl Glycols.—Divinyl glycol was prepared from acrolein by the method described previously[3] in the reduction of crotonaldehyde. The unsaturated glycol was hydrogenated with Adams platinum oxide catalyst[6] in 95% ethanol. After the catalyst was removed by centrifuging and the solvent removed by distillation, the melting point of the semi-solid residue was 50.4°. The solid was removed by filtration. Recrystallization from ligroin gave pure *meso*-diethyl glycol, m. p. 88.0–88.2°, m. p. of the bi-3,5-dinitrobenzoate, 190°.

The filtrate was fractionally distilled several times in a 3-foot long, adiabatic, metal spiral column at high reflux, until the lower boiling *dl*-isomer (b. p. 90.5–90.7° (8 mm.)) was obtained pure, m. p. 21.7°, m. p. of the bi-3,5-dinitrobenzoate, 167–168°. The melting point of this glycol did not increase upon redistillation or upon recrystallization from ligroin.

---

(1) Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2937 (1927).

(2) Lespieau and Weimann, *Compt. rend.*, **194**, 1946 (1932); **196**, 886 (1933).

(3) Young, Levanas and Jasaitis, THIS JOURNAL, **58**, 2274 (1936).

(4) van Risseghem, *Bull. soc. chim. Belg.*, **47**, 194 (1938).

(5) Kuhn and Rebel, *Ber.*, **60B**, 1565 (1927).

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

The Melting Point Diagram for the System *meso-dl*-Diethyl Glycol.—Known mixtures of pure *dl* and *meso* glycols sealed in small melting point tubes were heated slowly under constant agitation in a water-bath, the temperature of which was raised at the rate of 1° per five minutes. The temperatures at which the last particle of solid disappeared were recorded as the melting points and are plotted in Fig. 1. The composition of the eutectic mixture is 21.5% *meso*- and 78.5% *dl*-glycol and that of the glycol mixture (m. p. 50.4°) obtained from the hydrogenation of divinyl glycol 52% *meso* and 48% *dl*.

The divinyl glycol separated from the glycol mixture formed during the reduction of a mixture of acrolein and crotonaldehyde according to the method of Lespieau and Weimann[2] gave the same mixture of diethyl glycols as that from acrolein alone.

It may therefore be concluded that the pinacolic reduction of acrolein gives equal quantities of *meso*- and *dl*-divinyl glycol.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES, CALIFORNIA RECEIVED FEBRUARY 8, 1943

COMMUNICATIONS TO THE EDITOR

THE THERMODYNAMICS OF STYRENE (PHENYLETHYLENE), INCLUDING EQUILIBRIUM OF FORMATION FROM ETHYLBENZENE

Sir:

We have measured the heat capacity of styrene from 15 to 300°K., the heat of fusion, and the vapor pressure. The latter is represented between 0 and 60° by the equation

$$\log_{10} p_{\text{mm. Hg}} = -2604.67T^{-1} - 2.57692 \log_{10} T + 15.90485$$

The calculation of the entropy is summarized in Table I.

TABLE I

ENTROPY OF STYRENE

0–15°, 2 × $D(123/T)$	0.56	
15–242.47°, solid	36.82	
Fusion, 2617/242.47	10.79	
242.47–298.16°, liquid	8.61	
Liquid at 298.16°		56.78 ± 0.3 cal./deg. mole
Vaporization, 10390/298.16	34.85	
Compression, $R \ln 6.19/760$	−9.56	
Ideal gas at 1 atm.		82.07 cal./deg. mole

Since the reaction forming styrene from ethylbenzene is of considerable interest, we have calculated the equilibrium constant at various temperatures by thermodynamic methods. Measurements of the vapor pressure of ethylbenzene from 0 to 60° lead to the equation

$$\log_{10} p_{\text{mm. Hg}} = -2959.08T^{-1} - 5.8 \log_{10} T + 25.25883$$

and hence to a heat of vaporization of 10,100 cal./mole at 298.16°K. Combining this value with the observed pressure, 9.58 mm., and with the entropy of liquid ethylbenzene[1] we find for S^0_{298} 86.39 cal./deg. mole in the gas.

The heat of the reaction

$$C_6H_5CH_2CH_3 = C_6H_5CH{=}CH_2 + H_2$$

is calculable from the heats of hydrogenation of styrene and ethylbenzene.[2] Making reasonable assumptions regarding ΔC_p, we find for the temperature range 381–1000°K.

$$\log_{10} K = -5657.9T^{-1} - 6.3779 - 0.000804T + 4.3687 \log_{10} T$$

Values of the equilibrium constants calculated from this equation are tabulated in Table II.

TABLE II

DEHYDROGENATION OF ETHYLBENZENE TO FORM STYRENE

T, °K.	$-\log_{10} K$
381	10.26
400	9.48
500	6.30
600	4.15
800	1.41
1000	−0.27
(1500)	(−2.52)

Available data on the pyrolysis of ethylbenzene indicate that near-equilibrium yields were obtained at 425–550°,[3] but not at higher temperatures[4] where, however, the situation is obscured by numerous side reactions.

The details of the calorimetric work will be

---

[1] Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

[2] Dolliver, Gresham, Kistiakowsky and Vaughan, *ibid.*, **59**, 831 (1937).

[3] Sergienko, *Compt. rend. acad. Sci.* (U. R. S. S.), **26**, 69–72 (1940); Oblad, Marschner and Hurd, THIS JOURNAL, **62**, 2066 (1940).

[4] Dobryanskiĭ, Uchenyi, Zapiski, Leningrad, Gosudarst. Univ. im. A. S. Bubnova, Ser. Khem. Nauk I, No. 1, 105 (1935); Dobryanskiĭ, *et al.*, Trans. Exptl. Research Lab. "Khimgas," Materials on Cracking and Chem. Treatment of Cracking Products (U. S. S. R.), **3**, 1 (1936); Zal'kind and Bulavskiĭ, *Plasticheskie Massui*, No. 3, 9 (1935).