

three-necked flask equipped with a reflux condenser and motor stirrer. The temperature was maintained at  $-3$  to  $10^\circ$  during the total reaction time of seven hours. The mixture was decomposed by pouring into 100 cc. of hydrochloric acid and 100 g. of cracked ice. The upper layer was extracted with petroleum ether ( $28-38^\circ$ ), washed and dried.

After removal of the solvent and excess *o*-xylene, the product (44 g.) distilled at  $83-85^\circ$  (3 mm.). Fractionation of this material yielded 30.5 g. (70%) of 1,2-dimethyl-4-*t*-butylbenzene,  $n_D^{25}$  1.4970.

*Anal.* Calcd. for  $C_{12}H_{18}$ : C, 88.89; H, 11.11. Found: C, 88.83; H, 11.45.

**Oxidation of 1,2-Dimethyl-4-*t*-butylbenzene.**—The hydrocarbon (5 g.) was dissolved in 40 cc. of pyridine in a 3-necked conical flask and water added until the solution became slightly turbid. The flask was heated to  $80^\circ$  in a water-bath. Potassium permanganate (15 g.) was added with stirring during one hour and the mixture stirred an additional six hours. The manganese dioxide was separated by filtration. The filtrate was acidified with concentrated hydrochloric acid and the acid collected on a filter. Crystallization from dilute alcohol yielded 2 g. of white needles, m. p.  $140-141^\circ$ , the melting point recorded in the literature for 2-methyl-4-*t*-butylbenzoic acid.<sup>3,4</sup>

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.00; H, 8.33; n. e., 197. Found: C, 74.60; H, 8.44; n. e., 197.

**Alkylation of *o*-Xylene and Boron Trifluoride and *t*-Butyl Alcohol.**—*o*-Xylene (102 g.) and 19 g. of *t*-butyl alcohol were placed in a 500-cc. three-necked conical flask equipped with a motor stirrer, gas inlet and outlet tubes for the boron trifluoride. The boron trifluoride (14 g.) was added according to the procedure previously described.<sup>2</sup> The product was worked up in the usual manner; yield of 1,2-dimethyl-4-*t*-butylbenzene 34.5 g., b. p.  $76-81^\circ$  (3 mm.),  $n_D^{25}$  1.4970.

The acid obtained by oxidation of this hydrocarbon melted at  $139-140^\circ$  (n. e., 198) and did not depress the melting point of the acid described above.

(3) Effront, *Ber.*, **17**, 2333 (1884).

(4) Baur, *ibid.*, **33**, 2569 (1900).

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## Pyrazine-Water Azeotrope

By HARRY F. PFANN<sup>1</sup>

In the course of an investigation involving the purification of pyrazine by fractional distillation, it was observed that an azeotrope was formed with water. This was found to distil at  $95.5^\circ$  (uncor.) at 760 mm., to have a refractive index  $n_D^{25}$  1.4510, density of 1.06 at  $25^\circ$ , and a composition of 60% pyrazine—40% water. The mole ratio of 1:3.38 approaches the 1:3.31 ratio for the pyridine-water azeotrope, for which the boiling point is variously given as  $92.6-94.0^\circ$ .<sup>2,3,4</sup> The refractive index of pyrazine-water solutions appears to be a linear function of weight concentration. The pyrazine taken for this work had a melting range of  $50-52^\circ$  and boiling range  $114-115^\circ$ . Values in

(1) Present address: Koppers United Company, Butadiene Division, Monaca, Pa.

(2) E. Baud, *Bull. soc. chim.*, **5**, 1022-1033 (*C. A.*, **4**, 703 (1910)).

(3) Lange, "Handbook of Chemistry," 4th edition, p. 1210.

(4) Lecat, "La Tension de Vapeur des Melanges des Liquids," Brussels, 1913.

the literature<sup>5,6</sup> range from m. p.  $47-54^\circ$  and b. p.  $111-118^\circ$ .

The minimum boiling mixture was obtained from solutions containing an excess of either pyrazine or water. Essentially dry pyrazine resulted from fractionation of mixtures containing more than 60% pyrazine, the water being removed as the azeotrope. No azeotrope was observed with methyl or ethyl alcohols.

(5) Beilstein, Vol. XIII, p. 91.

(6) Aston, Peterson and Holowchak, *THIS JOURNAL*, **56**, 153-154 (1934).

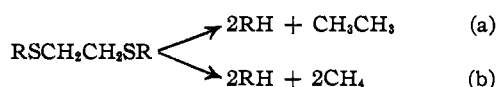
STAMFORD RESEARCH LABORATORIES  
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## Carbon-Carbon Cleavage in the Hydrogenolysis by Raney Nickel Catalyst of Ethylenedithiol and its Ethers

By H. R. SNYDER and GEORGE W. CANNON

In the determination of the structure of  $\omega, \omega'$ -bi-methionine [ $HO_2CCH(NH_2)CH_2CH_2SCH_2CH_2SCH_2CH_2CH(NH_2)CO_2H$ ] the *bis*-phenylhydantoin obtained from the substance was subjected to hydrogenolysis by Raney nickel catalyst.<sup>1</sup> This treatment converts a monosulfide ( $RSR'$ ) into the two molecules  $RH$  and  $R'H$ ,<sup>2</sup> and accordingly was expected to convert the *bis*-phenylhydantoin into two molecules of *dl*-3-phenyl-5-ethylhydantoin and one molecule of ethane. The first of these products was isolated in good yields.<sup>1</sup> However, analysis of the gas produced during the hydrogenolysis has shown that not only ethane but also methane is formed. The occurrence of these two hydrocarbons indicates that the hydrogenolysis of ethers of 1,2-dithiols may take two courses.



To determine whether carbon-carbon cleavage may be expected of other similar substances ethylenedithiol and certain of its ethers have been subjected to the hydrogenolysis. The hydrogenolyses were run as described by Mzingo, Wolf, Harris and Folkers<sup>2</sup> and the evolved gases were passed through a tower containing 20% aqueous sodium hydroxide into a liquid-air trap. At the end of each reaction the collection tube was connected momentarily to a vacuum pump while still immersed in liquid air, and the residual liquid was allowed to vaporize into gas sample tubes. The gas then was analyzed by standard methods.<sup>3</sup> The results are shown in the table.

(1) Snyder, Cannon, Howe and Nyman, *THIS JOURNAL*, **65**, 2211 (1943).

(2) Mzingo, Wolf, Harris and Folkers, *ibid.*, **65**, 1013 (1943).

(3) The authors are indebted to Mr. Cameron D. Lewis for certain of the gas analyses.