three-necked flask equipped with a reflux condenser and motor stirrer. The temperature was maintained at −3 to 10° 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°), washed and dried.

After removal of the solvent and excess *o*-xylene, the product (44 g.) distilled at 83–85° (3 mm.). Fractionation of this material yielded 30.5 g. (70%) of 1,2-dimethyl-4-*t*-butylbenzene, $n^{25}D$ 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° 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°, the melting point recorded in the literature for 2-methyl-4-*t*-butylbenzoic acid.[3,4]

Anal. Calcd. for $C_{12}H_{16}O_2$: 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.[2] The product was worked up in the usual manner; yield of 1,2-dimethyl-4-*t*-butylbenzene 34.5 g., b. p. 76–81° (3 mm.), $n^{25}D$ 1.4970.

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

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

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI
RECEIVED OCTOBER 4, 1943

Pyrazine–Water Azeotrope

BY HARRY F. PFANN[1]

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° (uncor.) at 760 mm., to have a refractive index $n^{25}D$ 1.4510, density of 1.06 at 25°, 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°.[2,3,4] 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° and boiling range 114–115°. Values in the literature[5,6] range from m. p. 47–54° and b. p. 111–118°.

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.

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[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.

[5] Beilstein, Vol. XIII, p. 91.

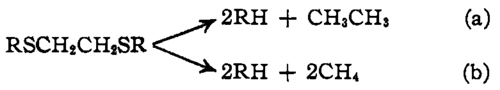
[6] Aston, Peterson and Holowchak, THIS JOURNAL, **56**, 153–154 (1934).

STAMFORD RESEARCH LABORATORIES
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT
RECEIVED OCTOBER 14, 1943

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 ω,ω′-bimethionine [$HO_2CCH(NH_2)CH_2CH_2SCH_2CH_2SCH_2CH_2CH(NH_2)CO_2H$] the *bis*-phenylhydantoin obtained from the substance was subjected to hydrogenolysis by Raney nickel catalyst.[1] This treatment converts a monosulfide (RSR′) into the two molecules RH and R′H,[2] 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.[1] 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.



$$RSCH_2CH_2SR \begin{cases} \nearrow 2RH + CH_3CH_3 & (a) \\ \searrow 2RH + 2CH_4 & (b) \end{cases}$$

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 Mozingo, Wolf, Harris and Folkers[2] 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.[3] The results are shown in the table.

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

[2] Mozingo, Wolf, Harris and Folkers, *ibid.*, **65**, 1013 (1943).

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

HYDROGENOLYSIS OF ETHYLENEDITHIOL AND CERTAIN OF ITS ETHERS

R in $RSCH_2CH_2SR$	Composition of hydrocarbon fraction of gas evolved, % Methane	Ethane
$HO_2CCH(NH_2)CH_2CH_2$—	34	66
CON(C_6H_5)COCHCH$_2$CH$_2$— └——NH——┘	44	56
$HOCH_2CH_2$—	0	100
C_6H_5—	23	77
H	14	86

In all five instances ethane was the major product, but in only one was it the sole product. Thus it is evident that carbon–carbon cleavage (reaction b) may occur as an important side reaction in the hydrogenolysis of derivatives of ethylenedithiol, but it is not yet possible to evaluate the structural factors which influence the two reactions (a and b).

CONTRIBUTION FROM THE NOYES LABORATORY
THE UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED NOVEMBER 15, 1943

Reaction of Diazomethane with α-Tetralone

BY R. B. THOMPSON[1a]

The ring expansion of cyclic ketones with diazomethane[1b] should be of considerable interest when applied to α-tetralone, since this system, stabilized by a fused ring, might permit preparation of more highly unsaturated compounds.

Although Burger and Mosettig reported that[2] α-tetralone did not react with diazomethane in ether, O. Pauli[3] found that the alcohol–sodium carbonate method gave a slow reaction yielding chiefly a mixture of ethylene oxides plus a ketonic fraction too small to identify.

The following experiments were carried out to investigate this reaction further: to 1 mole (146 g.) of α-tetralone, b. p. 87–88° (0.7 mm.) and $n^{20}D$ 1.5660, were added 130 cc. of absolute alcohol and 1.5 g. of finely powdered sodium carbonate and the temperature adjusted to 10–15°. Nitrosomethylurethan (246 g.) was added with stirring over a period of twenty-six to twenty-eight days, during which gas was regularly evolved.

After filtering, the low-boiling alcohol, water and methyl ethyl carbonate were distilled. Careful fractionation of the remainder gave 80–85% of unchanged α-tetralone, 7–8% of non-ketonic material, b. p. 93–96° (0.7 mm.) and 6–7% of a higher ketone, b. p. 103–106° (0.7 mm.).

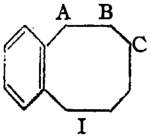
The ketone was crystallized by hydrolyzing the semicarbazone, which could not be obtained in a pure condition for analysis. The ketone then recrystallized from methyl alcohol melted at 73–75° and possessed a camphor-like odor.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 82.5; H, 8.4.

The ketone gave an oxime that after recrystallization from ethyl alcohol melted at 164–165°. In one instance an oxime melting at 89–90° was obtained.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.1; H, 8.0. Found: (165°) C, 76.4; H, 8.3; (90°) C, 75.9; H, 7.7.

These analytical data indicated that two methylene groups had been added to α-tetralone. Since diazomethane reacts with other cyclic ketones to give ring expansion, it is believed that this reaction has occurred here. Therefore, three structural formulas are possible, namely, those having the keto group at I-A, -B, or -C.



I

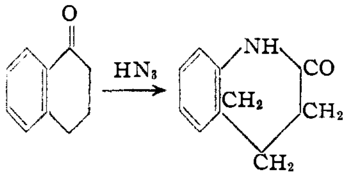
The structure has not been rigidly proved, but there is considerable evidence to show that it is IB.

Fry and Fieser[4] have prepared IC. It melts at 49–50° and gives an oxime melting at 112.5–114° while the ketone from the present experiment melts at 73–74° and gives an oxime melting at 165°.

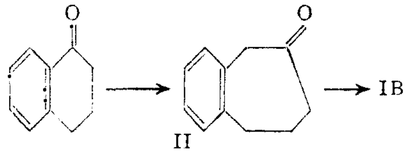
The following evidence tends to reject formula 1A. Mosettig and Jovanovic[5] found that diazomethane reacts with acetophenone to insert a methylene group next to the benzene ring.

$$C_6H_5COCH_3 \longrightarrow C_6H_5CH_2COCH_3$$

Briggs and DeAth[6] obtained the same results in the reaction of hydrazoic acid (the ammonia analog of diazomethane) with α-tetralone.



Since the reaction probably goes



it is easy to see why efforts to isolate II failed. Thus, α-tetralone, having the ketone group in the α-position, is relatively unreactive, but II, with a β-keto group, has an enhanced activity and will react as rapidly as formed. The final product IB is still a β-ketone but has lost most of its activity through resistance of the eight-membered ring to further expansion.[1b] Presumably, therefore, any higher ketones are present in quantities too small to be isolated from the mixture.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 20, 1943

[1a] Present address: Universal Oil Products Co., Riverside, Illinois.

[1b] Kohler, Tishler, Potter and Thompson, THIS JOURNAL, 61, 1057 (1939).

[2] Burger and Mosettig, *ibid.*, 53, 2295 (1931).

[3] Otto Pauli, Dissertation, Marburg (1935).

[4] Fry and Fieser, THIS JOURNAL, 62, 3489 (1940).

[5] Mosettig and Jovanovic, *Monatsh.*, 54, 427 (1929).

[6] Briggs and DeAth. *J. Chem. Soc.*, 456 (1937).