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
$CON(C_6H_5)COCHCH_2CH_2—$ with NH bridge	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
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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.).

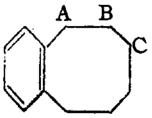
The ketone was crystallized by hydrolyzing the semicarbazone, which could not be obtained in a pure condition for analysis. The ketone then recrystallized from methyl alcohol melted at 73–75° and possessed a camphor-like odor.

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

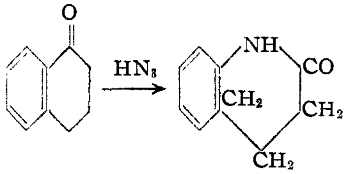
The structure has not been rigidly proved, but there is considerable evidence to show that it is IB.

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°.

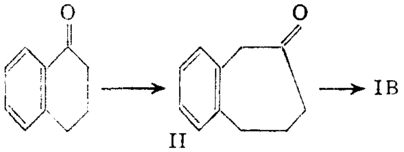
The following evidence tends to reject formula 1A. Mosettig and Jovanovic[5] found that diazomethane reacts with acetophenone to insert a methylene group next to the benzene ring.

$$C_6H_5COCH_3 \longrightarrow C_6H_5CH_2COCH_3$$

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



II

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.

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(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).