Then, with continuous stirring, the solution was heated at 150° for two hours. The solution became dark red; and on cooling, a tan solid was formed and no liquid remained. This solid is soluble in water and insoluble in ether or benzene. Recrystallization from ethylene dichloride gave a white solid, m.p. 88°, yield 96%.

Anal. Calcd. for $C_{16}H_{32}N_2O_4$: C, 60.7; H, 10.1; N, 8.8; mol wt., 316. Found: C, 60.2; H, 9.8; N, 9.2; mol. wt. (by Rast method), 323.

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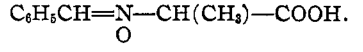
Phenyl-N-(1-carboxyethyl)-nitrone[1]

Hantzsch and Wild's synthesis[2] of phenyl-N-(carboxymethyl)-nitrone involved the condensation of β-benzaldoxime and chloroacetic acid. In the present work 2-bromopropionic acid was substituted for chloroacetic acid to form phenyl-N-(1-carboxyethyl)-nitrone,



$$C_6H_5CH{=}\underset{O}{N}{-}CH(CH_3){-}COOH.$$

To an aqueous solution of 5.6 g. of potassium hydroxide was added dropwise 2-bromopropionic acid to the discharge of phenolphthalein pink (8.8 ml. of acid). This solution was added to a mixture of 12.1 g. of β-benzaldoxime and 500 ml. of water in which was dissolved 5.6 g. of potassium hydroxide. The mixture was stirred at 100° until homogeneous, then was left on the steam-bath for 13 hours. When cool, it was acidified with hydrochloric acid. The white precipitate which formed was collected and washed with ether, in which it was insoluble. The aqueous filtrate was stored overnight at −10° and a further precipitation occurred. The combined precipitates weighed 3.3 g. After two recrystallizations from methanol, the product decomposed at temperatures varying with the rate of heating: rapid heating gave a decomposition temperature of 167–170°, while an attempt to dry the nitrone in an oven at 115° resulted in decomposition, accompanied by the odor of benzaldehyde.

Anal. (by V. Hobbs and J. Sorenson). Calcd. for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.75; N, 7.25. Found: C, 62.36; H, 5.63; N, 7.37.

The product was acidic. It did not reduce Fehling solution in the cold but did reduce it on brief heating. After heating the product with mineral acid, the cold reaction mixture reduced Fehling solution.

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[1] Investigation supported by a research grant from Swift and Company.

[2] A. Hantzsch and W. Wild, *Ann.*, **289**, 290, 305 (1896).

Derivatives of β-Hydroxypropyl Sulfides

N,N'-Bis-(2-hydroxy-3-methylthiopropyl)-1,2-diaminoethane.—A mixture of 14.5 g. of 69% 1,2-ethanediamine hydrate and 27.2 g. of 1-methylthio-2,3-epoxypropane was heated on a steam-bath to initiate reaction. After the reaction subsided, the mixture was refluxed for one hour. Liquid impurities were removed from the cooled, solidified reaction product by pressing between clay plates. The resulting material was recrystallized from ethyl acetate to give a white crystalline solid melting at 122–123°; yield 21% based upon the starting diamine.

Anal. Calcd. for $C_{10}H_{24}N_2O_2S_2$: N, 10.43. Found: N, 10.23.

N,N'-Bis-(2-hydroxy-3-ethylthiopropyl)-1,2-diaminoethane.—This white crystalline compound, prepared by the above method, melts at 118–119°; yield 22% based upon the starting diamine.

Anal. Calcd. for $C_{12}H_{28}N_2O_2S_2$: N, 9.44. Found: N, 9.29.

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COMMUNICATIONS TO THE EDITOR

THE REARRANGEMENT OF EPINOCHROME[1]

Sir:

We have reported the synthesis and isolation of crystalline epinochrome,[2] a dark-red crystalline compound of m.p. 78° by oxidative cyclization of epinine hydrochloride. This reaction is analogous to the oxidation of 3,4-dihydroxyphenylalanine to the "red pigment" in Raper's scheme of melanin formation. We now wish to report the spontaneous and the catalytic rearrangement of this crystalline compound into the colorless 5,6-dihydroxy-N-methylindole, an intramolecular oxidation–reduction which parallels the step in melanin formation where the "red pigment" is decolorized.

We have observed that this rearrangement takes place (A) spontaneously on standing of pure epinochrome at room temperature *in vacuo* in a sealed tube for several months when it has turned into a grayish white powder which essentially consists of 5,6-dihydro-N-methylindole; (B) on shaking the solution of epinochrome in water or in absolute methanol with palladium on charcoal in the presence of hydrogen or even in an atmosphere of pure nitrogen, when the solution becomes decolorized within a few minutes without the uptake of hydrogen. From the colorless solution more than 80% of the theoretical amount of 5,6-dihydroxy-N-methylindole m.p. 133° (reported 136°)[3] is isolated. *Anal.* Calcd. for $C_9H_9O_2N$: C, 66.12; H, 5.55; N, 8.57. Found: C, 66.41; H, 5.68; N, 8.85. Under the same conditions 2-carbethoxyepinochrome was decolorized without the uptake of hydrogen and with development of carbon dioxide.

The rearrangement of adrenochrome to 3,5,6-trihydroxy-*N*-methylindole ("adrenolutine")[4] bears a formal relationship to the rearrangement of

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[1] This work was supported by the Life Insurance Medical Research Fund.

[2] Sobotka and Austin, THIS JOURNAL, **73**, in press (1951).

[3] Harley-Mason, *J. Chem. Soc.*, 1276 (1950).

[4] Lund, *Acta Pharm. et Tox.*, **5**, suppl. 1, 75, 121 (1949).