the cyclic structure previously assigned to the quaternary ammonium salt but are satisfactorily explained on the basis of an open chain polymeric structure.

2. γ-Bromopropyldimethylamine has been found to give a similar polymer but a side reaction involving loss of hydrogen bromide occurs along with the simple polymerization reaction.

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Carbon Suboxide

BY CHARLES D. HURD AND FORREST D. PILGRIM

The most satisfactory method for the synthesis of carbon suboxide is the pyrolysis of diacetyltartaric anhydride, details for which have been given by Ott and Schmidt.[1] Yields of 41% (32 g. of the suboxide from an original 250 g.) were obtained when the vapors of the anhydride were distilled at 11 mm. over a hot platinum filament. The specially designed apparatus, which calls for difficult glass blowing, is, however, objectionable. In the present work it was found that even better yields could be realized with simple apparatus and at ordinary pressure.

Carbon suboxide was found to react readily with hydroxylamine, giving malonhydroxamic acid: $O{=}C{=}C{=}C{=}O + 2NH_2OH \longrightarrow CH_2(CONHOH)_2$. This is analogous to the synthesis of acethydroxamic acid from ketene[2] and hydroxylamine. In a similar way, β-phenylhydroxylamine reacted with carbon suboxide to produce N,N′-diphenylmalonhydroxamic acid, $CH_2(CON(C_6H_5)OH)_2$. No products were isolated wherein carbon suboxide and the hydroxylamine added to each other except in the ratio of 1:2.

Experimental Part

A Pyrex combustion tube (1 cm. inside diam.) was constricted at one end and sealed to the side arm of a 50-cc. Pyrex distilling flask[3] which carried a dropping funnel in the stopper. Previously the tip of the funnel had been drawn out to a capillary. The tube was then placed within an electric furnace (36 cm. long, but longer furnaces have also been employed satisfactorily). The tube was closed with a one-holed stopper into which fitted a bent tube leading downward into a flask. A two-holed stopper closed this flask. A vertical, water-cooled condenser was fitted into the other hole. From the top of the condenser, the gases were delivered into a receiver which was cooled to −78° by solid carbon dioxide and acetone. Any gases which were still uncondensed were passed through an aniline trap. The exhaust gases, which contained much carbon monoxide, were conducted into a hood or outdoors.

Fifty grams of diacetyltartaric anhydride, which was readily made by the method of

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[1] Ott and Schmidt, *Ber.*, 55, 2126 (1922); Ott, *ibid.*, 47, 2391 (1914).

[2] Hurd and Cochran, THIS JOURNAL, 45, 515 (1923).

[3] A larger flask could, of course, be used if desired.

Wohl and Oesterlin,[4] was placed in the distilling flask, melting the crystals within the flask whenever necessary. The empty reaction tube was then heated to a temperature of 625–650° and a salt-bath (or oil-bath) at 150° was placed around the distilling flask. Mercury was put in the dropping funnel and dropped at a constant rate into the molten anhydride. In this manner the latter was forced through the hot tube at a constant rate during two and a half hours. This gave a contact time in the hot zone of about fourteen seconds.

The liquid which was condensed by the water condenser weighed 33 g. By distillation these fractions were obtained: to 115°, 3.0 g.; 118–125° (acetic acid), 18.2 g.; 125–130°, 6.4 g.; residue, 5.4 g. No diacetyltartaric anhydride was recoverable from the residue.

The carbon suboxide[5] which was condensed in the −78° trap weighed 5.5–7.0 g. Another 0.8 g. was indicated since 2.5 g. of malonanilide was obtained from the aniline trap. This yield of 6.3–7.8 g. represents a yield of 35–49%. On redistillation shortly after its preparation, most of the product came over at 6–7°. A trace of hydroquinone, added to this distillate, was effective in retarding polymerization.

It was found advisable to remove the carbon deposit in the combustion tube fairly often, although not necessarily after each 50-g. run.

Carbon Suboxide and Hydroxylamine.[6]—One and a half cubic centimeters of liquid carbon suboxide was added dropwise to 1.8 g. of hydroxylamine,[7] the tube for which was kept in a bath at −15°. Each drop of the ketene caused a vigorous reaction. The product formed had the appearance of a yellow wax. With ferric chloride solution it gave an intense purple coloration, typical of hydroxamic acids. The solid was left in a vacuum desiccator over sulfuric acid for two days to remove the excess of hydroxylamine, after which it crystallized readily from hot water; m. p. 154–155° with decomposition. This is known[8] to be the melting point of malonhydroxamic acid, $CH_2(CONHOH)_2$. The yield was 1–1.5 g.

About 0.05 g. of the hydroxamic acid was dissolved in water and 2–3 drops of ammonium hydroxide added. After a short time, a copious precipitate of the characteristic acid ammonium salt separated. It melted with decomposition at 140°.

Carbon Suboxide and β-Phenylhydroxylamine

First.—A cold solution (0°) of 1.07 g. (0.01 mole) of β-phenylhydroxylamine in 5 cc. of ethyl acetate was added slowly to a cold solution of 0.7 cc. of carbon suboxide (0.01 mole) in 5 cc. of ethyl acetate. Crystals separated in about five minutes but the solution was left for an hour before filtering. The yield was about 1.2 g.; m. p. 128°.

Second.—This was like the first except that 2.14 g. (0.02 mole) of β-phenylhydroxylamine was taken with the 0.7 cc. of carbon suboxide. Crystals formed as before. Melting point, mixed melting point and analytical data showed that the products formed in the two cases were identical, namely, N,N′-diphenylmalonhydroxamic acid, $CH_2(CON(C_6H_5)OH)_2$.

Anal. Subs. 0.1997 (from first), 0.1939 (from second); CO_2, 0.4580, 0.4449; H_2O, 0.0820, 0.0803. Calcd. for $C_{15}H_{14}O_4N_2$: C, 63.0; H, 4.9. Found: C, 62.7, 62.6; H, 4.6, 4.6.

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[4] Wohl and Oesterlin, *Ber.*, **34**, 1144 (1901).

[5] This preparation has been confirmed several times in this Laboratory by Dr. R. K. Summerbell and Mr. G. W. Klingaman.

[6] Some preliminary work on this problem was performed by Mr. Fred W. Sackett in 1922.

[7] Prepared by the method of Hurd and Brownstein, THIS JOURNAL, **47**, 67 (1925).

[8] Hantzsch, Schatzmann and Urbahn, *Ber.*, **27**, 799, 803 (1894).

Summary

A simplified method is described for the synthesis of carbon suboxide from diacetyltartaric anhydride. Carbon suboxide reacts with hydroxylamine and with β-phenylhydroxylamine giving, respectively, malonhydroxamic acid and N,N′-diphenylmalonhydroxamic acid.

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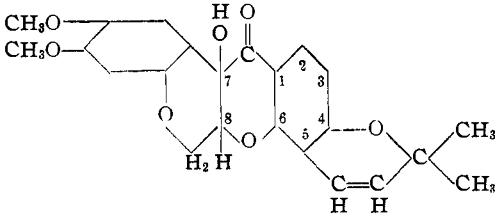
Tephrosin. III. Some Acidic Derivatives of Tephrosin

BY E. P. CLARK

Evidence has been presented[1] to show that tephrosin may be represented by formula I or the isomeric form in which the hydroxyl group is on carbon atom 8.



I. Tephrosin, $C_{23}H_{22}O_7$

An isomeric form of tephrosin has also been described,[2] and facts have been recorded indicating that the difference between the isomers must be sought in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8.

In this connection a hitherto unrecorded observation, which if anything confuses rather than clarifies the problem, should be presented.

In the first paper of this series,[3] tephrosindicarboxylic acid, m. p. 220°, was described. It was prepared by permanganate oxidation of tephrosin and was separated from the manganese dioxide as the potassium salt with the aid of boiling absolute alcohol. When the manganese dioxide remaining after the treatment with alcohol was again extracted with hot water, an isomeric tephrosindicarboxylic acid was obtained as the potassium salt. The free acid was obtained crystalline by acidifying the solution with a mineral acid.

When freshly crystallized and air dried the new acid melted at 127–128° and contained three mols of water of crystallization. Upon exposure to air for some time the melting point usually became 140–142°, but when it

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(1) Clark, THIS JOURNAL, **54**, 3000 (1932).

(2) Clark and Claborn, *ibid.*, **54**, 4454 (1932).

(3) Clark, *ibid.*, **53**, 729 (1931).