and aqueous sodium hydroxide, gave a yellow precipitate having an odor and melting point like that of iodoform. The material was not iodoform as shown by a mixed melting point.

This reaction has been studied using ω-cyanoacetophenone and found to produce the hitherto unreported triiodoacetonitrile along with benzoic acid. Triiodoacetonitrile is an unstable material, decomposing on standing to give iodine, cyanogen iodide, and an unidentified oil. Heating triiodoacetonitrile with aqueous sodium hydroxide produces carbon tetraiodide, ammonia, sodium carbonate, and an unidentified isocyanide.

Experimental

Preparation of Triiodoacetonitrile.—To a solution of 1.0 g. (0.0069 mole) of ω-cyanoacetophenone[1] in 30 ml. of 10% sodium hydroxide diluted to 100 ml. was added 5.3 g. (0.021 mole) of iodine and 10.0 g. of potassium iodide in 75 ml. of water. The yellow precipitate was sucked off, washed with water, and dried at 3° for fourteen hours. The product, 2.3 g. (80% yield) melted at 120–122° dec., and, when mixed with iodoform, melted at 110°. It was soluble in common organic solvents with liberation of iodine.

Anal. Calcd. for C_2I_3N: C, 5.7; H, 0.0; N, 3.3; I, 90.9. Found: C, 5.5; H, 0.06; N, 3.2; I, 90.4. Calcd. for diiodoacetonitrile, C_2HI_2N: C, 8.2; H, 0.34; N, 4.8; I, 86.7.

The product, stable when wet, was unstable dry but could be dried under carbon dioxide or nitrogen. Washing the wet product with aqueous potassium iodide also increased its stability during drying. Triiodoacetonitrile, dried by any of the above methods, decomposed on standing to give iodine, a brown oil, and white needles of cyanogen iodide, which sublimed from the decomposition mixture—m. p. 132–133°; recorded,[2] 146.0°.

Anal. Calcd. for ICN: C, 7.8; H, 0.0; N, 9.2; I, 83.0. Found: C, 8.1; H, 0.2; N, 9.3; I, 80.0.

With quinoline in ether, the cyanogen iodide gave a complex melting at 102–103°; recorded, 104°.[3]

The filtrate from the triiodoacetonitrile preparation gave 1.134 g. crude and 0.461 g. pure (or 55%) benzoic acid which did not depress the melting point of an authentic sample.

Triiodoacetonitrile and Sodium Hydroxide.—One gram of triiodoacetonitrile in 25 ml. of 5% aqueous sodium hydroxide was heated at 60° for one hour with stirring. The reddish-orange solid was sucked off and steam-distilled to remove unchanged triiodoacetonitrile. The red solid remaining was sublimed at 130–140° under 1–2 mm. pressure, giving crystals of carbon tetraiodide.

Anal. Calcd. for CI_4: C, 2.3; H, 0.0; N, 0.0; I, 97.7. Found: C, 2.6; H, 0.05; N, less than 0.1; I, 97.1.

The filtrate above gave a positive test for ammonia, carbonate ion, and an isocyanide by odor and by acid hydrolysis to formic acid.

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(1) Prepared by the method of Arndt and Loewe, *Ber.*, **71**, 1630 (1938).

(2) Cook and Robinson, *J. Chem. Soc.*, 1002 (1935).

(3) Mumm and Bruhn, *Ber.*, **68**, 176–183 (1935).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS
RECEIVED AUGUST 2, 1947

Purification of Thianaphthene

BY CORWIN HANSCH

In the preparation of thianaphthene by the reduction of 3-thianaphthenol[1,2] with zinc and acetic acid, thianaphthene is obtained which does not have a sharp melting point and apparently contains small amounts of 2,3-dihydrothianaphthene. Refluxing thianaphthene thus prepared with 10% by weight of sulfur for four hours, then isolating the product by steam distillation from a dilute sodium hydroxide solution, gives thianaphthene melting sharply at 32°.

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(1) Friedländer, *Ber.*, **41**, 231 (1908).

(2) Hansch and Lindwall, *J. Org. Chem.*, **10** 381 (1945).

POMONA COLLEGE
CLAREMONT, CALIFORNIA
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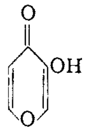
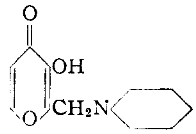
A Synthesis of Maltol

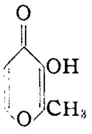
BY M. A. SPIELMAN AND MORRIS FREIFELDER

Maltol (III) has been isolated from pine needles,[1] larch bark,[2] the destructive distillates of various organic materials[3] and the alkaline hydrolysis products of streptomycin.[4] However, no synthesis has been reported.

We have condensed pyromeconic acid (I) with piperidine and formaldehyde to give the Mannich base (II). There was no evidence of a second condensation such as takes place with kojic acid, a similar 3-hydroxy-4-pyrone.[5] Hydrogenation of the base over a palladium catalyst gave maltol (III) in poor yield. Meconic and pyromeconic acids have been made artificially,[6] and the total synthesis of maltol is therefore complete.


I


II


III

Experimental[7]

3-Hydroxy-2-piperidinomethyl-4-pyrone.—To 3.5 g. of pyromeconic acid in 20 ml. of alcohol was added 2.8 ml. of piperidine and 1.4 ml. of 40% aqueous formaldehyde. There was a mild heat of reaction after which the mixture was heated for five minutes on the steam-bath. It was cooled, acidified with ethereal hydrogen chloride, diluted with two volumes of ether and left in the cold for several hours. The precipitate was recrystallized from 1:5 alcohol–acetone. The yield of pure hydrochloride, m. p. 193–195° with foaming, was 2.8 g. and 0.5 g. of less pure product, m. p. 189–190°, was recovered from the mother liquors.

Anal. Calcd. for $C_{11}H_{16}ClNO_3$: N, 5.70. Found: N, 5.73.

The free base was prepared with the aid of silver carbonate. It is very soluble in the usual organic solvents except petroleum ether. After two crystallizations from benzene–petroleum ether, it melted at 125–126°.

Anal. Calcd. for $C_{11}H_{15}NO_3$: N, 6.69. Found: N, 6.61.

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(1) Feuerstein, *Ber.*, **34**, 1804 (1901).

(2) Peratoner and Tamburello, *ibid.*, **36**, 3407 (1903).

(3) Brand, *ibid.*, **27**, 806 (1894); Kiliani and Bazlen, *ibid.*, **27**, 3115 (1894); Erdmann and Schaefer, *ibid.*, **43**, 2398 (1910); Reichstein and Beitter, *ibid.*, **63**, 824 (1930); Goos and Reiter, *Ind. Eng. Chem.*, **38**, 132 (1946).

(4) Schenck and Spielman, THIS JOURNAL, **67**, 2276 (1945).

(5) Woods, *ibid.*, **68**, 2744 (1946).

(6) Peratoner, *C. A.*, **6**, 994 (1912); Thoms and Pietrulla, *Ber. pharm. ges.*, **31**, 4 (1921); Wibaut and Kleipool, *Rec. trav. chim.*, **66**, 24 (1947).

(7) Microanalyses by E. F. Shelberg.