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.

---

(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°.

---

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

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

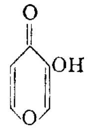
POMONA COLLEGE
CLAREMONT, CALIFORNIA RECEIVED JULY 10, 1947

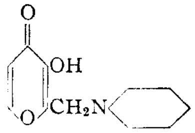
A Synthesis of Maltol

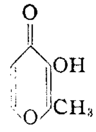
BY M. A. SPIELMAN AND MORRIS FREIFELDER

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.

---

(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.

Maltol.—To 189 mg. of the above hydrochloride in 10 ml. of water was added 1 ml. of *N* sodium hydroxide and 50 mg. of palladium-on-charcoal catalyst. It was shaken twenty hours at 25° under 20 mm. more than atmospheric pressure of hydrogen. The absorption was 1.05 molar equivalents. The solution was acidified with hydrochloric acid and extracted several times with chloroform. Evaporation of the chloroform left a gummy brown solid from which maltol was isolated by sublimation at 130° followed by crystallization from benzene. The yield was 7 mg., m. p. and mixed m. p. 160–162°.[8]

Anal. Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.48; H, 4.76.

Many hydrogenations were conducted, and the above is typical. The highest yield of maltol (17%) was obtained when the Mannich base hydrochloride was hydrogenated in absolute alcohol over palladium-on-charcoal at 100° and 100 atmospheres pressure. Adams platinum oxide catalyst and Raney nickel led to no maltol whatever. Chemical reduction with sodium methoxide[9] also failed.

The benzoate of synthetic maltol was prepared with benzoyl chloride in pyridine. It melted at 112–113° and the mixed m. p. was 113–114°.

---

(8) We are indebted to The Cliffs Dow Chemical Corporation of Marquette, Michigan, for a sample of pure maltol from wood distillates.

(9) Cornforth, Cornforth and Robinson, *J. Chem. Soc.*, 682 (1942); Woodward and Doering, This Journal, **67**, 863 (1945).

Abbott Laboratories
North Chicago, Illinois

Received July 11, 1947

On the Correlation of the Spectroscopic and Thermal Energy Differences between the Fluorescence and Phosphorescence Levels of Dye Molecules

By M. Kasha and R. E. Powell

A general interpretation of the fluorescence and phosphorescence properties of polyatomic molecules on the basis of potential curve crossing suggests a limitation in the validity of the mechanism of luminescence of dyes proposed by Jablonski.[1] Whereas the scheme proposed by Jablonski uses a line energy level diagram, the new interpretation involves a radiationless intersystem "crossing" of potential curves for the first two electronic states above the ground state,[2] as shown in the figure. The potential curves as drawn represent time-average cross-sections, of the potential energy hypersurfaces for the electronic states, along the critical coördinate involved in the excitation of the triplet state[3] of the molecule. An analysis of the rates of the various processes occurring in the S′ state led to the conclusion that for a maximum probability of interaction[4] between the S′ and T states, the "crossing" must occur at the lowest point of the upper curve.

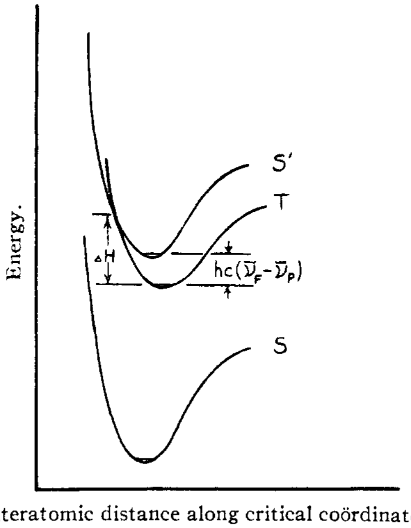


Fig. 1.—Schematic potential energy curves for the three lowest electronic states of a dye molecule.

According to the line energy level scheme of Jablonski, the spectroscopic energy difference between the zero-point energy levels of the fluorescent (unstable) and phosphorescent (metastable) states of a dye should be equal to the heat of activation required for lifting molecules from the phosphorescent to the fluorescent state. This theorem apparently was confirmed by the experiments of Lewis, Lipkin and Magel,[5] in which the fluorescence–phosphorescence energy difference for acid fluorescein dye in boric acid glass was found spectroscopically to be 9 kcal., while the heat of activation as determined by the temperature coefficient of the alpha process[6] of phosphorescence was found to be 8 ± 1 kcal.

However, according to the mechanism of excitation of the phosphorescent state based on potential curve crossing, the two experimental energy quantities may differ considerably in magnitude, if the point of crossing is not at the lowest point of the upper curve. This is shown in the figure, which compares schematically the two energy values for a case of high crossing. According to this picture, the heat of activation should equal or exceed the spectroscopic difference between the zero-point levels of the fluorescent and phosphorescent states.

For the best demonstration of this lack of correlation between the two energy values, (a) the dye should have as small an interval as possible between the zero-point levels of the S′ and T states, and (b) the emission spectra should have

---

(1) A. Jablonski, *Z. Physik*, **94**, 38 (1935).

(2) M. Kasha, *Chem. Rev.*, in process of publication.

(3) The triplet state theory of phosphorescence as developed by Lewis and Kasha (This Journal, **66**, 2100 (1944); **67**, 994 (1945)) is assumed in this treatment, although metastability of an electronic level may be due to various causes. However, the spectroscopic and magnetic studies of the phosphorescent state conducted in this laboratory have given strong evidence that the relatively long-lived, temperature-independent luminescence (β-phosphorescence) occurring 2000 to 12,000 cm.$^{-1}$ lower than the normal absorption band is, in general, due to a triplet–singlet transition.

(4) In the absence of heavy or paramagnetic atoms, and strong fields.

(5) Lewis, Lipkin and Magel, This Journal, **63**, 3005 (1941).

(6) α-Phosphorescence involves a T–S′ thermal activation, followed by S′–S emission. Thus, although relatively long-lived, its spectrum is identical with the normal fluorescence spectrum. β-Phosphorescence corresponds to spontaneous T-S emission.