centration of flavin-adenine dinucleotide in the lantern than in the rest of the firefly's tissues. Also the concentration of this flavin coenzyme in the lantern, 36–70 γ per gram of dry weight, is one-fourth to one-half that found in liver, which is one of the tissues richest in flavin-adenine dinucleotide in the mammalian organism. It is, therefore, not unreasonable to suspect that flavin-adenine dinucleotide may play some role in the luminescent mechanisms of the firefly.

DEPARTMENT OF BIOLOGICAL CHEMISTRY
HARVARD UNIVERSITY MEDICAL SCHOOL
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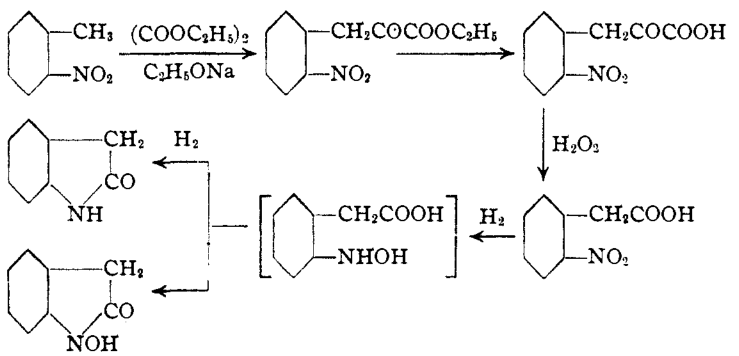
Synthesis of Oxindole

BY FREDERICK J. DI CARLO

The catalytic hydrogenation of *o*-nitrophenylacetic acid with Adams catalyst has been found to give oxindole in good yield. The starting acid was prepared by a modification of the method of Mayer and Balle.[1] It has been shown that ethyl *o*-nitrophenylpyruvate, which is formed by the condensation of ethyl oxalate with *o*-nitrotoluene, distills with steam. Consequently it was necessary to hydrolyze this ester completely before steam-distilling the excess *o*-nitrotoluene. This led to an increase of about 50% in the yield of *o*-nitrophenylpyruvic acid.

The oxidation of *o*-nitrophenylpyruvic acid to yield *o*-nitrophenylacetic acid has been reported.[1,2] Best results were obtained by the oxidation of a neutral solution with 3% hydrogen peroxide.



When the hydrogenation of *o*-nitrophenylacetic acid was carried out slowly in the presence of a small quantity of catalyst, an appreciable amount of 1,2-dioxindole was isolated. The hydrogenation of 1,2-dioxindole under similar conditions was ineffective. This suggests the formation of a hydroxylamine intermediate capable of concurrent slow ring closure to 1,2-dioxindole and rapid hydrogenation (followed by ring closure) to oxindole.

***o*-Nitrophenylpyruvic Acid.**—A mixture of 43.8 g. (0.3 mole) of ethyl oxalate and 41.1 g. (0.3 mole) of *o*-nitrotoluene was poured into a cooled solution of 6.9 g. of sodium in 80 cc. of absolute alcohol. The mixture was refluxed for ten minutes. The volume was doubled by adding water and refluxing was continued for one and one-half hours in order to hydrolyze the ethyl *o*-nitrophenylpyruvate. Unreacted *o*-nitrotoluene was then recovered by steam distillation. The residue was cooled, acidified with hydrochloric acid and vigorously shaken in order to cause crystallization of the oil which separated. The *o*-nitrophenylpyruvic acid was filtered off, washed with water and dried; yield, 44 to 51 g. of crude product, m. p. *ca.* 115°. After treatment with charcoal and crystallization from water, the acid melted at 119–120°.

Oxindole.—A solution of 18.1 g. (0.1 mole) of *o*-nitrophenylacetic acid in 180 cc. of glacial acetic acid was subjected to hydrogenation at an initial pressure of 50 lb. per sq. in. in the presence of 0.2 g. of platinum oxide. When the reduction was complete (twenty minutes), the catalyst was removed by filtration and washed with a small portion of glacial acetic acid. After distillation of the solvent under diminished pressure, the residue was triturated with a solution of sodium carbonate, filtered and washed with water. The product was crystallized from water and 11.3 g. (88%) of oxindole was obtained as white needles, m. p. 127–129°.

Anal. Calcd. for C_8H_7NO: N, 10.52. Found: N, 10.60.

1,2-Dioxindole.—The hydrogenation of a solution of 18.1 g. of *o*-nitrophenylacetic acid in 180 cc. of glacial acetic acid in the presence of 0.05 g. of platinum oxide required several hours and a poorer yield of oxindole was obtained (75%). Acidification of the sodium carbonate washings with hydrochloric acid caused the precipitation of a mixture of *o*-nitrophenylacetic acid and 1,2-dioxindole. The former was removed with dilute sodium bicarbonate solution; 0.9 g. (m. p. 143.5°) separated upon addition of hydrochloric acid. The 1,2-dioxindole was treated with charcoal and twice recrystallized from water; 1.0 g. was obtained in the form of glistening plates, m. p. 198–199° A mixed melting point with the product prepared by the method of Reissert[2] showed no depression. 1,2-Dioxindole reduced Fehling solution on heating.

Anal. Calcd. for $C_8H_7O_2N$: N, 9.39. Found: N, 9.30.

When 0.1 g. of platinum oxide was employed, the hydrogenation required forty-five minutes. The yield of oxindole was 85% and 0.2 g. of pure dioxindole was isolated. Use of 0.02 g. of platinum oxide caused but little reduction within twenty-four hours and 80% of the *o*-nitrophenylacetic acid was recovered.

Brucine Salt of 1,2-Dioxindole.—1.8 g. of brucine was added to a warm solution of 0.75 g. of 1,2-dioxindole in methyl alcohol. The salt separated and was crystallized from ethyl alcohol; cubic crystals, m. p. 223°. Its aqueous solution became intensely blue upon the addition of a drop of ferric chloride solution.

Anal. Calcd. for $C_{31}H_{33}O_6N_3$: N, 7.73. Found: N, 7.77.

A solution of 2.5 g. of 1,2-dioxindole in 250 cc. of glacial acetic acid was subjected to hydrogenation for six hours in the presence of 0.05 g. of platinum oxide at an initial pressure of 50 lb. per sq. in. The solvent was distilled under reduced pressure and the residue was dissolved in a warm solution of sodium carbonate. Acidification of the carbonate solution resulted in the separation of 2.3 g. of pure 1,2-dioxindole.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
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Esterification of Fatty and Amino Acids with 1,2-Epoxides in Aqueous Solution

BY HEINZ FRAENKEL-CONRAT AND HAROLD S. OLCOTT

It has recently been shown[1] that 1,2-epoxides

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[1] Mayer and Balle, *Ann.*, **403**, 188–189 (1914).

[2] Reissert, *Ber.*, **30**, 1043 (1897); **41**, 3924 (1908).

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[1] Fraenkel-Conrat, *J. Biol. Chem.*, **154**, 227 (1944).