(150 ml) was added to the reaction mixture, followed by ascorbic acid (25 g). The system was shaken for several minutes until all the red color was discharged. The ether layer was separated, dried (Na_2SO_4), and concentrated, under nitrogen, to about 30 ml. Dry benzene (50 ml) was added and the solution concentrated under reduced pressure, at ca. 30°, (nitrogen "leak") to about 30 ml. This solution was then filtered and *n*-heptane (100 ml) added to the filtrate; a flocculent white precipitate was obtained, which was purified by dissolving in warm benzene (35°), reprecipitating with *n*-heptane giving 5,6-dihydroxy-*N*-methylindole (0.7 g; 57%) m.p. 131–132° in long colorless needles. Recrystallization of a sample from *n*-heptane raised the melting point to 133–134°. The melting points quoted for (III) in the literature range from 133° to 136° (refs. 1–6). However, the product obtained by the current procedure was sufficiently pure for most purposes.

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Psychiatric Research Unit,
University Hospital,
Saskatoon, Saskatchewan.

A CONVENIENT PREPARATION OF TRYPTOPHOL

Thomas Nogrady and Terrence W. Doyle

Trytophol, 3-indolylethanol, is of considerable interest as an intermediate in indole chemistry. Its preparation in larger amounts is, however, not too convenient with the existing methods, and yields are sometimes poor.

Usually, it is prepared by the LAH reduction of ethyl 3-indolyl-acetate, in a near-quantitative yield. The ester, however, is rather difficult to obtain, through gramine, its methosulphate, indolylacetonitrile, and indolylacetic acid. This 6-step synthesis gives an overall yield of 59% only (cf. (1)).

The new procedure of Johnson and Crosby (2) makes indolylacetic acid available at a 90% yield, and from this acid tryptophol, in an overall yield of 79%, can be obtained. This method requires the use of a concentrated potassium hydroxide solution, and a heating period of 14–22 hours at 250° in an autoclave.

The reduction of ethyl indolylacetate suffers from the disadvantage that it has to be conducted at −20°, otherwise the reaction mixture becomes a tough gum which is impossible to stir.

In the method of Elderfield and Fischer (3) the indolylglyoxylyl chloride is obtained in one step from the indole, according to Speeter and Anthony (4). The chloride is then directly reduced by LAH in tetrahydrofuran at room temperature, and gives an overall yield of 74%. This elegant procedure, described for the 6-methoxy derivative, gave unsatisfactory yields and an impure product when applied to unsubstituted indolyl-3-glyoxylyl chloride.

Therefore, we prepared ethyl 3-indolylglyoxylate from the chloride (4), by the action of ethanol, in the presence of triethylamine. The crude ester, obtained in a 95% yield and showing the melting point reported in the literature (5) was reduced with LAH in tetrahydrofuran to give tryptophol in a 95% yield. The overall yield from indole is therefore 85–86%.

EXPERIMENTAL

Melting points were taken in capillaries in a Gallenkamp aluminum block, and are corrected. Infrared spectra were determined in KBr disks on a Beckman IR8 grating instrument.

Ethyl 3-indolylglyoxylate

3-Indolylglyoxylyl chloride (4), 10.35 g (0.05 moles), was refluxed for 30 minutes in a mixture of 60 ml absolute ethanol and 5.30 g (7.2 ml, 0.052 moles) of triethylamine. The reaction mixture was chilled, and the crystals were filtered and washed with a little ethanol. Yield 7.60 g (70.0%), m.p. 186–187° (lit. m.p. 186°) (5).

The mother liquid was evaporated under reduced pressure, and the residue triturated with water. On filtration, an additional 2.70 g (25.0%) ester was obtained, m.p. 184–186°.

Infrared absorption (λ_{max}, μ): 3.11 (NH, vs), 3.37 (C—H, w), 5.87 (C═O, s), 6.20 (C═C, s), 7.95 (C—O, s).

3-Indolylethanol (Tryptophol)

Ethyl indolylglyoxylate (10.85 g (0.05 moles)) was refluxed for 2 hours with 6.6 g (0.175 moles) $LiAlH_4$ in 200 ml dry tetrahydrofuran, with mechanical stirring. We then added 20 ml water slowly while cooling the reaction mixture in ice water. The precipitate was filtered and washed several times with tetrahydrofuran, and the solvent evaporated after drying over Na_2SO_4. The white crystalline residue weighed 6.50 g (95.0%), m.p. 54–55°.

It can be recrystallized from benzene–petroleum ether, m.p. 56–58° (lit. m.p. 58–59° (6)).

Infrared absorption (λ_{max}, μ): 2.94 (NH, OH, vs), 3.40, 3.43, 3.50 (C—H, w), 6.20 (C═C, w), 9.52 (OH, s, broad).

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DEPARTMENT OF CHEMISTRY,
LOYOLA COLLEGE,
MONTREAL 28, QUE.

H_0 ACIDITY FUNCTIONS FOR NITRIC AND PHOSPHORIC ACID SOLUTIONS CONTAINING ADDED SODIUM PERCHLORATE

DONALD G. LEE AND ROSS STEWART

In connection with an investigation of the mechanism of the chromic acid oxidation of alcohols (1) we required the values of the Hammett acidity function, H_0, for nitric and phosphoric acid solutions containing equimolar amounts of sodium perchlorate and acid. The functions were determined by use of weak bases for indicators in the manner described by Paul and Long (2).

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