THE TRITYLATION OF INDOLE

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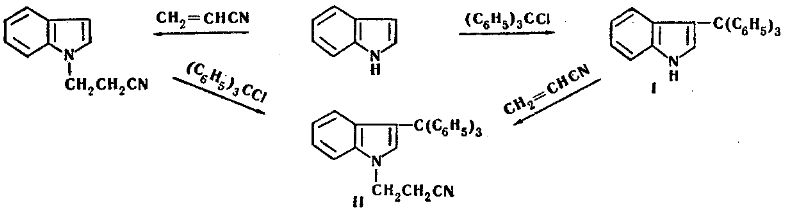
Contrary to information in the literature, the reaction of indole with chlorotriphenylmethane forms not N-tritylindole but β-tritylindole.

In 1936, Japanese chemists [1] showed that the reaction of indole with chlorotriphenylmethane in pyridine gives a substance with a melting point of 211-212°C to which they ascribed the structure of N-tritylindole. When we repeated the experiment described we did in fact obtain a substance with the same melting point. However, a deeper study of this product has shown that it is not N-tritylindole but β-tritylindole (I).

The Japanese workers themselves observed that when indolylmagnesium iodide reacted with chlorotriphenylmethane the same substance with mp 211.5-212°C was formed. As is well known, in the Grignard reaction indole gives β-substituted derivatives.

The cyanoethylation of indole in the N- and β- positions takes place under different conditions [2,3]. The cyanoethylation of compound I that we performed gives N-(β-cyanoethyl)-β-tritylindole (II). Its structure was shown by tritylating N-(β-cyanoethyl)indole with chlorotriphenylmethane.



The hydrolysis of the nitrile II gives N-(β-carboxyethyl)-β-tritylindole (III).

It is known that on brief heating in acetic acid, N-tritylated derivatives unlike C-tritylated derivatives undergo detritylation. When compounds I, II and III were boiled with 75% acetic acid for half an hour, no detritylation reaction took place and the starting materials were recovered.

Compound II withstood heating at 160°C for five hours without change. When it was heated at about 280°C, a mixture of decomposition products was formed among which the decyanoethylation product—compound I – was found. As is well known, the β-cyanoethyl group can be split out if it is attached to the nitrogen atom of indole but is stable if it is present in the β position [3].

The IR spectrum of compound I in the solid state has a strong absorption band in the 3437 cm^{-1} region, which corresponds to the NH group.

EXPERIMENTAL

β-Tritylindole (I). A mixture of 2.3 g (20 mmoles) of indole and 5.6 g (20 mmoles) of chlorotriphenylmethane in 20 ml of dry pyridine was boiled for 2 hr. The product was isolated as described in the litera-

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ture [1]. The yield of the indole was 5.4 g (75%). mp 211-212°C. Found, %: N 4.12, 4.02. Calculated for $C_{27}H_{21}N$, %: N 3.89.

N-(β-Cyanoethyl)-β-tritylindole (II). a. With stirring, 0.09 g (1.5 mmole) of caustic potash was slowly added to a mixture of 5.4 g (15 mmoles) of I and 1.6 g (30 mmoles) of acrylonitrile in 30 ml of dry benzene, and the mixture was boiled for 2 hr. After cooling, the solution was filtered, and the solvent was evaporated in vacuum. The residue was treated with ethanol. The yield of the nitrile II was 4.8 g (79%). mp 157-158°C. Found, %: N 7.00, 6.88. Calculated for $C_{30}H_{24}N_2$, %: N 6.77.

b. The experiment was carried out with 1.7 g (10 mmoles) of N-(β-cyanoethyl)indole [2], 2.8 g (10 mmoles) of chlorotriphenylmethane, and 10 ml of dry pyridine. The reaction and the isolation of the tritylation product were carried out as for the preparation of the indole I. The yield of the nitrile II was 2.5 g (56%). Mp 157-158°C. A mixture with the material obtained by method (a) showed no depression of the melting point.

N-(β-Carboxyethyl)-β-tritylindole (III). A mixture of 2 g of the nitrile II and 15 ml of 10% ethanolic caustic potash was boiled for 4 hr. Then, with cooling, the reaction mixture was gradually treated with hydrochloric acid until it had an acid reaction to Congo Red. The acid III that deposited was recrystallized from ethanol. Yield 2.0 g (93%). mp 223-224°C. Found, %: N 3.16, 3.20. Calculated for $C_{30}H_{25}NO_2$, %: N 3.23.

LITERATURE CITED

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