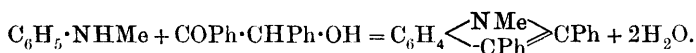


LXXV.—*Preparation of Substituted Indoles from Benzoin and Secondary Arylamines.*

By MARION BROCK RICHARDS.

JAPP AND MURRAY (Trans., 1894, **65**, 889) showed that by heating benzoin with primary arylamines, in presence of zinc chloride or of the hydrochloride of the amine, 2:3-diphenylindoles could be prepared.

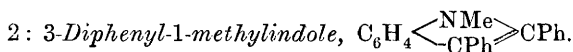
The author now finds that, by employing secondary in place of primary arylamines, analogous indoles may be obtained. Thus, by the interaction of benzoin and methylaniline, in presence of zinc chloride or of methylaniline hydrochloride, 2:3-diphenyl-1-methylindole is formed, according to the equation:



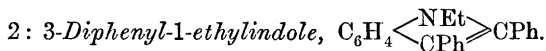
In like manner, by employing other secondary arylamines, other similar diphenylindoles have been prepared.

In the account of the experimental results, only that method of preparation is described which gave the best yield. In the case of the phenylnaphthylamine compounds, the yield by both methods was poor, but the product of the preparation in which the hydrochloride was used was much more easily purified. In this case, too, a variation in the method had to be introduced, the hydrochlorides of the phenylnaphthylamines being so unstable as to be decomposed by water. By conducting the experiment in an atmosphere of hydrogen chloride, the reaction was enabled to proceed by the momentary formation of the hydrochloride.

EXPERIMENTAL.



A mixture of 10.6 grams of benzoin, 16 grams of methylaniline, and 7.2 grams of methylaniline hydrochloride was heated to its boiling point until no more water was given off. The product was dissolved in benzene, and the solution, after being extracted with hydrochloric acid, was distilled under diminished pressure. The distillate, which passed over at about 280°, crystallised from glacial acetic acid in clusters of colourless needles (Found, C=88.88; H=6.13; N=4.95. Calc., C=89.05; H=6.01; N=4.95 per cent.), melting at 137° (Bischler and Fireman, *Ber.*, 1893, **26**, 1345, give 139°).

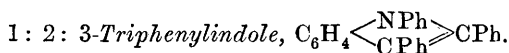


This was prepared by the same method as the preceding indole. The proportions employed were 10.6 grams of benzoin, 18 grams of ethylaniline, and 7.9 grams of ethylaniline hydrochloride. The product was treated in the same way. The distillate crystallised from alcohol in slender, colourless prisms, melting at 132.7°:

0.2046 gave 0.6679 CO₂ and 0.1188 H₂O. C=89.03; H=6.45.

0.2618 „, 10.8 c.c. N₂ (moist) at 16° and 752 mm. N=4.76.

C₂₂H₁₉N requires C=88.89; H=6.40; N=4.71 per cent.

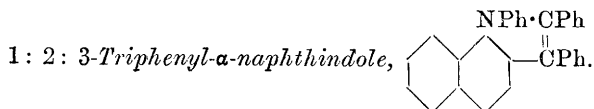


Twenty-one grams of benzoin, 25 grams of diphenylamine, and 30 grams of zinc chloride were heated until water ceased to be evolved, the product being treated exactly as in the previous cases. The distillate crystallised from glacial acetic acid in small, white, glistening laminæ, and from alcohol in voluminous masses of minute needles, melting at 186°:

0.2003 gave 0.6650 CO_2 and 0.1016 H_2O . $\text{C}=90.55$; $\text{H}=5.64$.

0.2408 „ 8.6 c.c. N_2 (moist) at 17° and 753.5 mm. $\text{N}=4.11$.

$\text{C}_{26}\text{H}_{19}\text{N}$ requires $\text{C}=90.43$; $\text{H}=5.51$; $\text{N}=4.06$ per cent.



21.2 Grams of benzoïn and 32.9 grams of phenyl- α -naphthylamine were heated in an oil-bath at 250° for about four hours in a continuous current of hydrogen chloride. The product was dissolved in glacial acetic acid, and the crystals which separated, after recrystallisation from acetic acid, gave very light, colourless needles, melting at 253° . Distillation of the mother liquor under diminished pressure yielded only benzoïn and phenyl- α -naphthylamine:

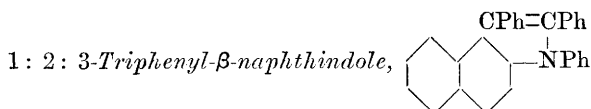
0.2082 gave 0.6938 CO_2 and 0.1006 H_2O . $\text{C}=90.88$; $\text{H}=5.37$.

0.3452 „ 10.5 c.c. N_2 (moist) at 17° and 743.7 mm. $\text{N}=3.46$.

$\text{C}_{30}\text{H}_{21}\text{N}$ requires $\text{C}=91.14$; $\text{H}=5.32$; $\text{N}=3.54$ per cent.

In the formation of this compound the condensation has been assumed to take place with the naphthyl rather than with the phenyl group, thus yielding a naphthindole instead of an indole. This is more in accordance with the greater mobility of the hydrogen atoms of naphthalene as compared with those of benzene.

As sodium does not act on an ethereal solution of 1 : 2-diphenyl- α -naphthindole, it was not possible to obtain the compound just described through the agency of bromobenzene.



This was prepared in the same way as triphenyl- α -naphthindole, the same weights of the corresponding substances being taken. The product, crystallised from acetic acid, yielded colourless needles, melting at 172.5° . On distilling the mother liquor under diminished pressure, a further quantity of substance was obtained from the distillate which passed over above the range of the thermometer (360°):

0.2038 gave 0.6802 CO_2 and 0.0981 H_2O . $\text{C}=91.03$; $\text{H}=5.35$.

0.3391 „ 10.7 c.c. N_2 (moist) at 18° and 764 mm. $\text{N}=3.66$.

$\text{C}_{30}\text{H}_{21}\text{N}$ requires $\text{C}=91.14$; $\text{H}=5.32$; $\text{N}=3.54$ per cent.

With regard to the constitution of this compound, the same assumption has been made as in the case of the foregoing triphenyl-

α -naphthindole. Moreover, it has been assumed that the compound is an $\alpha\beta$ -naphthalene derivative, the well-known difficulty of forming $\beta\beta$ -derivatives of naphthalene rendering the latter constitution improbable.

This research was suggested by Professor Japp and carried out under his supervision, and the author wishes to thank him for the interest he has always taken in the work.

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