

Free radical Cyclisation of Diphenylamine; a Convenient Synthesis of Carbazole and 3-Methylcarbazole

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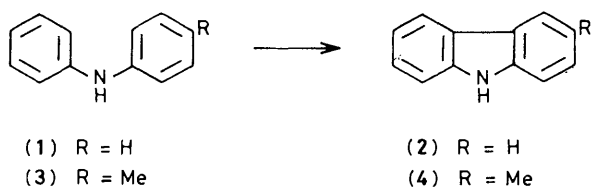
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Diphenylamine was cyclised to carbazole in moderate yield in refluxing chloroform with benzoyl peroxide in the presence of light (200 W tungsten lamp); 3-methylcarbazole was synthesised similarly.

The cyclisation of diphenylamine to carbazole is known to proceed at red heat in very poor yield; photolytic methods also bring about this cyclisation,^{1,2} which also occurs³ on heating diphenylamine with I₂ at 350 °C, presumably *via* a free-radical pathway.⁴ Benzoyl peroxide is a well known radical generator at moderate temperature, and we now report that diphenyl-

amine (**1**) cyclises to form carbazole (**2**) with benzoyl peroxide in presence of light.

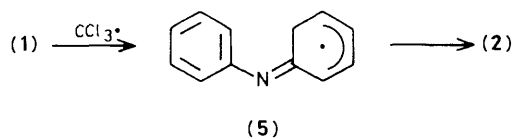
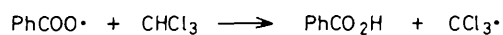
Diphenylamine (**1**) was heated with benzoyl peroxide in refluxing chloroform (green solution) in the presence of light (200 W tungsten lamp) for 6 h. The solution was treated with aqueous NaHCO₃, and the chloroform layer washed, dried,



concentrated, and chromatographed over neutral alumina. Elution with benzene furnished carbazole (2), m.p. 242 °C (40% yield), which was identified by comparison with an authentic specimen.

3-Methylcarbazole (4) was also obtained from the diphenylamine derivative (3) in the same way (40% yield). The product, m.p. 208 °C, was identical with a sample of (4) isolated from *Clausena heptaphylla*.⁵

The cyclisation does not take place in the dark under otherwise similar conditions, nor was carbazole detected with carbon tetrachloride as solvent, suggesting that the $\text{CCl}_3\cdot$ radical is first generated under the reaction conditions. Chloroform is the most suitable solvent. The reaction is presumed to proceed *via* the intermediate π radical (5). The failure of *N*-methyl-diphenylamine to undergo cyclisation under similar conditions favours this proposition.



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