Photocyclisation of Diphenylamines. Synthesis of Glycozoline

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IRRADIATION of solutions of diphenylamines with ultraviolet light leads to changes in the ultraviolet and fluorescence spectra, which have been shown to be due to the formation of carbazoles.[1] Photocyclisation of diphenylamines has now been found to offer a convenient preparative route to some carbazole derivatives. Thus irradiation of a dilute solution (approx. 0·005 M) of 2-methyldiphenylamine in petroleum (b.p. 40—60°) through quartz with light from a mercury-vapour lamp afforded 1-methylcarbazole in 60—70% yield after 12 hr., m.p. 119—120° (lit. 121°), λ_{max} (EtOH) 240, 250, 260, infl. 286, 295, infl. 318, 328, 340 mμ; log ϵ, 4·64, 4·52, 4·33, 4·03, 4·20, 3·52, 3·61, 3·56. Similarly 2,2′-dimethyldiphenylamine was smoothly converted into 1,8-dimethylcarbazole, m.p. 49—50°. Reactions were generally conducted in air or in presence of a small amount of iodine, but an oxidant is evidently not required, for cyclisation was equally well effected in an atmosphere of nitrogen (*cf.* Bowen and Eland[1]).

Polymethylcarbazoles, which are sometimes troublesome to prepare by other routes, are readily available in appropriate cases by photocyclisation. Thus 1,2,7,8- and 1,3,6,8-tetramethylcarbazole, which were required for comparison with two tetramethylcarbazoles isolated from a petroleum fraction, were so obtained in good yield (m.p. and mixed m.p. with the petroleum specimens 201—202° and 142—143° respectively) by irradiation of the corresponding tetramethyldiphenylamines. The 1,2,7,8-tetramethylcarbazole was accompanied by some of the 1,2,5-trimethyl derivative (m.p. 145°) formed by displacement of a methyl group during cyclisation.[2] Under the same conditions *N*-phenyl-β-naphthylamine was unchanged.

The alkaloid glycozoline, from *Glycosmis pentaphylla* (Retz) DC, has been assigned the structure 3-methoxy-6-methylcarbazole.[3] The synthetic compound was readily obtained by photocyclisation of 4-methoxy-4′-methyldiphenylamine, and after purification by chromatography on alumina formed plates m.p. 179° (lit. 181—182°), λ_{max} (EtOH) 229, infl. 244, 255, 266, infl. 300, 308, 349, 362 mμ; log ϵ, 4·48, 4·25, 4·10, 3·97, 4·14, 4·28, 3·51, 3·48, τ ($CDCl_3$) 7·5 (singlet 3H), 6·1 (singlet 3H), 2·6—3·0 (multiplet 5H), 2·1 and 2·4 (two singlets, 1H each). The picrate formed wine-coloured needles, m.p. 177—178° (lit. 182°).

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[1] C. A. Parker and W. J. Barnes, *Analyst*, 1957, **82**, 606; E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 1963, 202; K.-H. Grellman, G. M. Sherman and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 1881.
[2] *Cf.* W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.*, 1965, 6221.
[3] D. P. Chakraborty, *Tetrahedron Letters*, 1966, 661.