

## 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.<sup>1</sup> 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°),  $\lambda_{\max}$  (EtOH) 240, 250, 260, infl. 286, 295, infl. 318, 328, 340 m $\mu$ ; log  $\epsilon$ , 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<sup>1</sup>).

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.<sup>2</sup> Under the same conditions *N*-phenyl- $\beta$ -naphthylamine was unchanged.

The alkaloid glycozoline, from *Glycosmis pentaphylla* (Retz) DC, has been assigned the structure 3-methoxy-6-methylcarbazole.<sup>3</sup> 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°),  $\lambda_{\max}$  (EtOH) 229, infl. 244, 255, 266, infl. 300, 308, 349, 362 m $\mu$ ; log  $\epsilon$ , 4.48, 4.25, 4.10, 3.97, 4.14, 4.28, 3.51, 3.48,  $\tau$  (CDCl<sub>3</sub>) 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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<sup>1</sup> 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.

<sup>2</sup> *Cf.* W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.*, 1965, 6221.

<sup>3</sup> D. P. Chakraborty, *Tetrahedron Letters*, 1966, 661.