Tetrahedron Letters,Vol.25,No.47,pp 5429-5430,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

A SIMPLE ROUTE TO INDOLE-2,3-QUINODIMETHANE - A FACILE SYNTHESIS OF CARBAZOLES

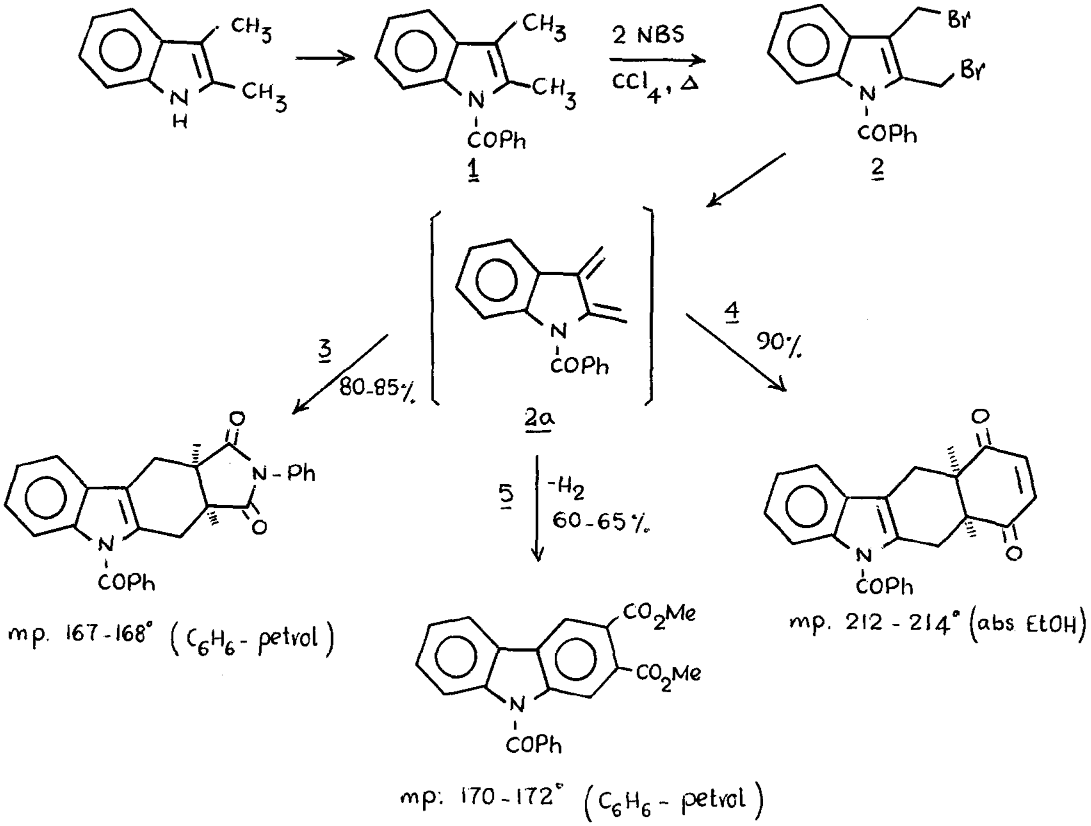
B.Saroja and P.C.Srinivasan*

Department of Organic Chemistry, University of Madras

A.C.College Campus, Madras-600 025, India.

Abstract : 2,3-Dimethylindole is easily converted into N-benzoyl-2,3-dibromo methylindole, the latter upon treatment with sodium iodide in DMF in the presence of a suitable dienophile furnishes a carbozole derivative.

Indole-2,3-quinodimethanes have been the target of recent studies[1a,b] and a new strategy for the synthesis of aspidosperma alkaloids involving this intermediate has been reported[1c]. In continuation of our studies with the synthetic uses of N-protected bromomethylindoles[2], we report here the preparation of N-benzoyl-2,3-dibromomethylindole which could be used for the generation of indole-2,3-quinodimethane. Treatment of 2,3-dimethylindole with molar equivalent of sodium hydride (THF, 40-50°, N_2 atm) and benzoylation of the resulting N-sodio derivative (PhCOCl, 0-5°, 2 hr, 64° - 24 hrs) afforded the N-benzoyl-2,3-dimethylindole 1 as light yellow crystals (mp. 87°, 37-40%, Lit[3] 98°) after chromatography (silica gel - petrol) of the crude product. Bromination of 1 following the published procedure[2] gave N-benzoyl-2,3-dibromomethylindole 2 in 80-85% yield (mp. 148°, benzene-petrol) after conventional work up. It was observed that the quinodimethane can easily be generated from 2 and trapped by suitable dienophiles (N-phenylmaleimide 3, p-benzoquinone 4 and dimethyl acetylenedicarboxylate 5) in dry DMF. Addition of finely powdered sodium iodide to a solution of 2 and the dienophile in equimolar amounts in DMF at 50-55° resulted in an immediate appearance of dark red colour and the reaction mixture was maintained at that temperature for 3 hours. Then the DMF was removed under reduced pressure and the crude product after digestion with an aqueous sodium thiosulphate solution was crystallised from appropriate solvent. All compounds gave satisfactory spectral and analytical data. Work is in progress to use this reaction to synthesize analogs of medicinally important carbazole alkaloids.



The authors thank Dr.M.V.Lakshmikantham, Department of Chemistry, University of Pennsylvania, USA for valuable suggestions, Dr.B.J.Heywood, M & B Co. England for Mass spectra and UGC, Government of India for a fellowship to B.S. under FIP Scheme.

References :

1. a) E.R.Marinelli, Tetrahedron Lett., 2745 (1982).
   b) M.G.Saulnier and G.W.Gribble, ibid, 5435 (1983).
   c) T.Gallagher and P.Magnus, J.Amer.Chem.Soc., 105, 2086 (1983) and references cited therein.
2. M.Vedachalam, B.Mohan and P.C.Srinivasan, Tet. Letters, 3531 (1983)
3. S.G.P.Plant and M.L.Tomlinson, J.Chem.Soc., 955 (1933).

(Received in UK 29 August 1984)