SYNTHESIS OF INDENO[1,2-<u>b</u>]INDOLE BY FLASH VACUUM PYROLYSIS OF 2-PHENYLQUINOLINE-3,4-DICARBOXYLIC ANHYDRIDE

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Summary: Flash vacuum pyrolysis of 2-phenylquinoline-3,4-dicarboxylic anhydride at 800°C/0 06 Torr gave indeno[1,2-<u>b</u>]indole This was reduced to form 5,10-dihydroindeno[1,2-b]indole and it added nucleophiles to give dihydroindenoindoles with the 10-substituents Ph, NEt₂, OMe, Me, CH(COOMe)₂, and CMe₂NO₂

Cyclopentadienylidenecarbenes which are in equilibrium with benzynes at high temperatures¹ can undergo intramolecular trapping² An example of this process is the flash vacuum pyrolysis (f v p) of 3-phenylnaphthalene-1,2-dicarboxylic anhydride (1) at 960°C/O 04 Torr which yields indeno[2,1-a]indene (2) in 95% yield ³



We now report the first such ring contraction applied to the heterocyclic ring of quinoline in a synthesis of indeno[1,2-<u>b</u>]indole(4) Attempts to make (4) by conventional methods have so far been unsuccessful⁴

2-Phenylquinoline-3,4-dicarboxylic acid was prepared from isatin and methyl benzoylacetate using a modification of the procedure described by Engelhard⁵, and the acid was converted into the anhydride (3) (m p 206-7°) by treatment with acetic anhydride F v p of (3) at 800°C/0 06 Torr with trapping of the pyrolysate on a cold finger condenser cooled with liquid nitrogen gave a red pyrolysate (*ca* 30% as C₁₅H₉N) on the condenser and dark material at the exit from the furnace The red pyrolysate was shown to be indeno[1,2-b]indole (4) by spectroscopic measurements⁶ and by conversion into derivatives of 5,10-dihydroindeno[1,2-b]indole (5)

(Scheme 1).



(5a) X=H (H₂, Pd/C or LiAlH₄), (5b) X=Ph (PhLi), (5c) X=NEt₂ (HNEt₂), (5d) X=OMe (NaOMe/HOMe), (5c) X=Me (MeMgl), (5f) X=CH(CO₂Me)₂ (NaCH(CO₂Me)₂), (5g) X=CMe₂NO₂ (NaCMe₂NO₂) Yields were 17-29% based on (3)

The indenoindole (4) was stable in chloroform or ether at low temperatures but decomposed during several hours at room temperature. The residual red solid obtained on evaporation of the solvent also darkened and decomposed over several hours. Compound (4) when washed directly onto palladised carbon with ether and hydrogenated gave only 4% yield of 5,10-dihydroindeno[1,2-b]indole (5a) but reduction with lithium aluminium hydride in ether gave (5a) in 18% yield (from (3)). For the remaining reactions, compound (4) was washed from the condenser directly into the reagent with ether under an atmosphere of nitrogen. The products and the reagents are given in Scheme (1). Products (5a) 7, (5b) 8 and (5c) 4a were identified by comparison of their spectroscopic properties with those of the known compounds. The remaining compounds (5d-5g) showed the expected analytical and spectroscopic properties 9 .

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- 6 Molecular ion, *m*/z 203 073 ± 0 002 C₁₅H₉N requires 203 073 v_{max} (Nujol) 1626 w, 1605 w cm⁻¹ ¹H n m r spectrum, δ (CDCl₃, 200MHz) 7 19-6 69, m, 8H, aromatic, 6 41, s, 1H λ_{max} (Et₂O) nm (log ε) 268 (4 73), 276 (4 87), 308 (3 45), 388 (3 60), 400 (3 59), 409 (3 73), 424 (3 46), 436 (3 58) Mass spectrum, *m*/z 203 (M, 100%), 176 (7), 102 (12), 88 (9), 75 (7)
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- 9 (5d) m p 93-95° v_{max} 3402 cm⁻¹ ¹H n m r δ (CDCl₃, 300 MHz) 3 28, s, OMe, 5 55, s, H10 (5e) 159-61° 3394 cm⁻¹ δ 1 60, d, Me, 3 93, q, H10 (5f) 147-48° 3412, 1748 cm⁻¹ δ 3 77, s, 3 64, s, 2 x OMe, 3 70, d, CH(COOMe)₂, 4 71, d, H10 (5g) 163-65° 3405 cm⁻¹ δ 1 30, s, 1 80, s, 2 x Me, 4 82, s, H10

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