Chemistry of Heterocyclic Compounds, Vol. 30, No. 1, 1994

LETTERS TO THE EDITOR

1,2-MIGRATION OF THE BENZYL GROUP IN INDOLES

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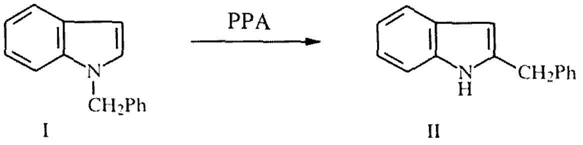
3-Alkyl and 3-arylindoles rearrange to the corresponding 2-substituted indoles in acid media [1,2]. The driving force for this rearrangement is thought to be the increased basicity of the 2-substituted indole and the consequent stability of its cation in comparison with that of the 3-substituted indole [2]. If this is true then 1,2-migration of these substituents should be possible in acid media since, for example, a 2-alkylindole is more basic than the 1-alkylindole. We have encountered a rearrangement of this type.

When an attempt was made to synthesize 2-alkyl-1-benzylindoles by rearrangement of the corresponding 3-alkyl-1-benzylindoles by heating in polyphosphoric acid (PPA) by the method described previously [2] a mixture of isomeric indoles was formed. Apart from the expected 2-alkyl-1-benzylindole, the reaction mixture contained 3-alkyl-2-benzylindole. The two isomers were obtained by concurrent 3,2- and 1,2-migration of the substituents. We carried out the isomerization of 1-benzylindole (I) to observe the 1,2-migration in pure form and to verify its preparative potential. Heating 1-benzylindole in PPA gave 2-benzylindole (II) in 74% yield.



A mixture of 200 mg 1-benzylindole I, prepared by the reaction of indole with benzyl chloride with interphase catalysis [3], and 4 ml PPA was heated at 140°C for 20 h. The cooled reaction mixture was treated with ice water and extracted with ether. The ether layer was separated, washed with $NaHCO_3$ solution and water, dried over $MgSO_4$, and the solvent evaporated. The residue was crystallized from a 5:1 hexane–benzene mixture to give indole II (148 mg, 74%), m.p. (dimorphism) 73-75°C immediately after crystallization or melting, and 85-86°C one day after crystallization (m.p. 75 and 85°C [4]). R_f 0.28 (Silufol, 10:1 hexane–ether). ^{1}H NMR spectrum (250 MHz, $CDCl_3$): 7.72 (1H, br. s, NH), 7.54, 7.26 and 7.08 (1H, m; 6H, m and 2H, m respectively, protons of the benzene ring), 6.28 (1H, br.s, NH), and 4.08 ppm (2H, s, CH_2). Mass spectrum, *m/z* (%): 207 (100, M^+), 206 (61), 204 (13), 130 (84), 129 (25), 103 (12), 77 (20), 63 (15), 51 (28), 50 (13).

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0009-3122/94/3001-0121$12.50