SYNTHESIS OF N-HETEROPOLYCYCLIC AROMATICS FROM 3-ARYL-1-AZIRINES BY THERMAL RING EXPANSION

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Novel and selective synthesis of N-heteropolycyclic aromatic compounds by thermal ring expansion of 3-aryl-1-azirines are reported.

On thermal treatment of 2-methyl-3-(1-naphthyl)-1-azirine (1) at 140°C for 24 hr. gave 2-methyl-3H-benz[e]indole (4). 2-Methyl-1H-benz[g]indole (5) was selectively formed from 2-methyl-3-(2-naphthyl)-1-azirine (2); another possible isomeric product, 2-methyl-1H-benz[f]indole (6) was not detected. Under the same conditions, 2-methyl-3-(1-methyl-2-naphthyl)-1-azirine (3) was intact. But heated at 170°C for 66 hr. (3) gave mainly 3-methylbenz[h]isoquinoline (7) and small amounts of 1-methyl-2-phenethylnaphthalene (10) and 1-(1-methyl-2-naphthyl)-2-propanone (9).

Selective formation of (5) in preference to (6) was explained by the stabilities of the respective benzindolenine precursors. The decreased reactivity of (3) was ascribed to the steric hindrance and/or the lower migratory aptitude of methyl group relative to that of hydrogen. Thermolysis of vinyl azides, which were the precursors of (1) and (2), also gave the same products. On the same manner, 1,4-di(2-azido-2-carbethoxyethenyl)benzene (14) gave 2,7-dicarbethoxy-1,8-dihydrobenzo[2,1-b; 3,4-b]dipyrrole (15).