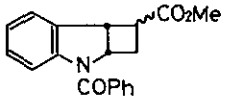
RING TRANSFORMATION OF INDOLES: SYNTHESIS OF 1H-1-BENZAZEPINES

Masazumi Ikeda, Toshiko Uno, Kazunori Ohno, and Yasumitsu Tamura
Faculty of Pharmaceutical Sciences, Osaka University
133-1, Yamada-kami, Suita, Osaka, Japan

Synthesis of 3-substituted 2a,7b-dihydrocyclobuta[b]indoles (3) and their ring-expansion reaction to 1H-1-benzazepines are described. By applying the method of Jurian and coworkers, photoadduct (2) was obtained as a mixture of the stereoisomers from 1-benzoylindole (1) and methyl acrylate in 67% yield. Alkaline hydrolysis of (2) followed by oxidative decarboxylation with lead tetraacetate gave 3-benzoyl-2a,7b-dihydrocyclobuta[b]indole (3a), mp 190-191°, in 23% yield. Lithium aluminum hydride reduction of (3a) in ether at room temperature afforded a mixture of (3b) and N-benzyl derivative (3c) in ca. 2:1 ratio. Since (3b) was a labile compound, the mixture was directly treated with acetic anhydride and ethyl chloroformate to give the N-acetyl (3d), mp 94-95° (lit. mp 94-95°), and N-carbethoxy derivatives (3e), mp 54-55° (lit. an oil), each in 60% yield, respectively, in addition to the N-benzyl derivative (3c) (30%).

The possibility of rearrangement of (3) to the valence isomer, 1H-1-benzazepines, was examined. When heated at 270-280° for 10 min without solvent, (3a) gave oily 1-benzoyl-1H-1-benzazepine (4) (major) and N-benzoyl-1-naphthylamine (5) (minor) as an unseparable mixture (73%), along with (1)(4%) and (3a) (23%). At higher temperature (300°), (3a) gave (5) as a sole product. *Compounds (3d) and (3e) were stable at 270-280°.* The ring expansion of (3a) to (4) was found to be catalyzed by silver ion. Thus, refluxing a solution of (3a) in xylene in the presence of silver fluoroborate for 10 hr gave a mixture of (4) (58%) and the starting material (3a). Prolonged heating did not change the product ratio.

Preliminary study of the chemical properties of 1H-1-benzazepine (4) revealed close similarity to 2-substituted 1-acyl-1H-azepines.



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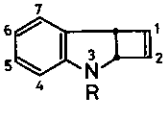
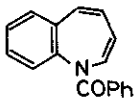


3a, R=COPh
3b, R=H
3c, R=CH2Ph
3d, R=COCH3
3e, R=CO2Et



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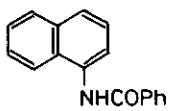

5