A STUDY OF THE BENZYNE REACTION BETWEEN 1-HALOGENOBENZYL- AND PHENETHYL-2-BENZAZEPINE AND DIMSYLSODIUM

Shinzo Kano, Tsutomu Yokomatsu, and Shiroshi Shibuya
Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji , Tokyo 192-03

1-(2-Bromo-4,5-dimethoxyphenethyl)-1,2,3,4-tetrahydro-7,8-dimethoxy-2-methyl-5H-2-benzazepine (13) underwent a novel ring expansion, on treatment with dimsylsodium, to give trans-13,14-methanodibenz[b,f]azecine (14) and the cis-isomer (15). The reaction of 1-(2-bromo-4,5-dimethoxyphenethyl)-1,2,3,4-tetrahydro-8-hydroxy-7-methoxy-2-methyl-5H-2-benzazepine (16) with dimsylsodium also gave the similar results. On the other hand, 1-(2-bromo-4,5-dimethoxyphenethyl)-1,2,3,4-tetrahydro-7-hydroxy-8-methoxy-2-methyl-5H-2-benzazepine (19) afforded the dibenz[b,g]azacycloundecine (20) under the similar conditions. Treatment of 1-(2-bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-7,8-dimethoxy-5H-2-benzazepine (23) with dimsylsodium yielded the indole derivatives (24) and (25).

Furthermore, a reaction between 1-(2-bromo-4,5-dimethoxybenzyl)-1,2,3,4-tetrahydro-7-hydroxy-8-methoxy-2-methyl-5H-2-benzazepine (26) was also examined to give the 5,6,7,8-tetrahydrodibenz[b,f]azecine (29) possessing a trans double bond at the 13,14-position together with formation of the 14-(methylsulfinyl)-methyldibenz[b,f]azecine (30). The similar reaction using 1-(2-bromo-4,5-dimethoxybenzyl)-1,2,3,4-tetrahydro-7,8-dimethoxy-2-methyl-5H-2-benzazepine (27) afforded the 5,6,7,8-tetrahydrodibenz[b,f]azecine (33) possessing a cis double bond at the 13,14-position. A reaction of 1-(2-bromo-4,5-dimethoxybenzyl)-1,2,3,4-tetrahydro-8-hydroxy-7-methoxy-2-methyl-5H-2-benzazepine(28) with dimsylsodium also showed a similar ring expansion to give dibenz[b,f]azecine derivatives.