SYNTHESES OF DIBENZO[b,f]AZONINE AND DIBENZO[b,g]AZECINES THROUGH RING TRANSFORMATION

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The benzyne reaction of 1-(2-bromo-4,5-dimethoxyphenethyl)-1,2,3,4-tetrahydro-6-hydroxy-7-methoxy-2-methylisoquinoline(21) using sodium dimsyl afforded 5,6,7,12,13,14-hexahydro-10-hydroxy-7-methansulfinylmethyl-2,3,9-trimethoxydibenzo[b,g]azecine(22). This product was previously assigned to 5,6,7,8,9,10-hexahydro-3-hydroxy-8-methansulfinylmethyl-2,12,13-trimethoxy-7-methyldibenzo[e,g]azecine(25a), which was revised to (22). Reductive deoxigenation of (22) with Zn-Hg gave 7-(methylthio)methyl derivative(23) whose desulfurization yielded 7-methyldibenzo[b,g]azecine(24). The similar reaction using 1-(2-bromo-4,5-methylenedioxyphenethyl)- and 1-(3-bromo-4-methoxyphenethyl)-1,2,3,4-tetrahydro-6-hydroxy-7-methoxy-2-methylisoquinoline also examined to give the corresponding dibenzo[b,g]azecines(28) and (29), respectively. These 7-methansulfinylmethyldibenzo[b,g]azecines were converted to 7-methyldibenzo[b,g]azecines through deoxigenation of (28)and (29),followed by desulfurization of 7-(methylthio)methyl derivatives (30) and (31). The structure of (30) was confirmed by comparison of the spectroscopic data with those of the authentic specimen alternatively synthesized.

This ring transformation reaction was applied to the formation of 6-substituted dibenzo[b,g]azonines from the 1-halogenobenzyl-6-hydroxyisoquinolines.