

HETEROCYCLIC COMPOUNDS
DERIVED FROM DIHYDROCOUMARIN DERIVATIVES

Tsuguo Tanaka and Takashi Tomimatsu

Faculty of Science and Technology, Saga University

Honjo, Saga-chi 840

The reaction of 6-methyl-, and 6-chloro-dihydrocoumarin with BBr_3 yielded 6,6'-dimethyl- and 6,6'-dichloro-2,2'-spirobichroman in 16 and 15 % yield, respectively, while 6,8-dimethyldihydrocoumarin gave 15.6 % yield of 1,5-bis-(2-hydroxy-3,5-dimethyl)pentan-3-one which was converted into 6,6',8,8'-tetramethyl-2,2'-spirobichroman. Structures of these compounds were identified by the syntheses starting with 5-methyl-, 5-chloro-, and 3,5-dimethyl-salicylaldehyde.

6,6'-Dimethyl-2,2'-spirobichroman on refluxing with AcOH-HBr-HI for 16 hours rearranged into 4,4'-dihydroxy-7,7'-dimethyl-1,1'-spirobiindane, the structure of which was identified by the synthesis starting with 5-methylsalicylaldehyde via condensation with acetone, methylation, catalytic reduction with Pd-C, cyclization with $\text{POCl}_3\text{-SnCl}_4$, and demethylation.

The reaction of 6-methyl-, and 6-chloro-dihydrocoumarin with N-methylformanilide and POCl_3 gave compounds having molecular formulas $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$, and $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}_4\text{Cl}$, respectively.

Formulas including N-methyltetrahydroquinoline and aziridine structures were assigned to these compounds on the basis of their Raney-nickel catalytic reduction, LiAlH_4 reduction, and perbenzoic acid oxidation products.