Acid Catalyzed Condensation of Isoprene with Orcinol: Synthesis of 2,2-Dimethylchromans and 5-Methylxanthyletin Derivatives

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Condensation of orcinol with 2-methylbuta-1,3-diene (isoprene) has been achieved in the presence of orthophosphoric acid as catalyst leading to the exclusive formation of 2,2-dimethylchromans in one step. A novel route for the synthesis of 5-methylxanthyletin derivatives is described.

(Keywords: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone; 2,2-Dimethylchromans; 2-Methylbuta-1,3-diene; 5-Methylxanthyletin; Orcinol; Pechmann condensation)

Sauer katalysierte Kondensation von Isopren mit Orcin: Synthese von 2,2-Dimethylchroman- und 5-Methylxanthyletin-Derivaten

Kondensation von Orcin mit Isopren in Gegenwart von Orthophosphorsäure führt in einem Schritt zu 2,2-Dimethylchromanen. Außerdem wird ein neuer Weg für die Synthese von 5-Methylxanthyletinderivaten aufgezeigt.

Introduction

A frequently occurring arrangement of the isoprenoid unit in natural phenolic products is either in the form of the 2,2-dimethylchromene ring or as 3,3-dimethylallyl unit. 2,2-Dimethylchromans occur rarely in plants; they are, however, obtained as degradative products during the structural elucidation of naturally occurring phenolic products bearing isoprenoid unit. The utility of these chromans as synthetic precursors for 2,2-dimethylchromenes and pyranocoumarins has been well demonstrated. In view of this, the condensation of
1,3-dihydroxy-5-methylbenzene (orcinol) (1) with 2-methylbuta-1,3-diene in the presence of an acid catalyst (orthophosphoric acid) has been studied which resulted in the exclusive formation of 2,2-dimethylchromans in good yields compared with earlier methods for their synthesis. Further, the natural occurrence of linear pyranocoumarins (xanthyletin derivatives) and their marked physiological activities prompted us to devise a new and convenient route for their synthesis. In the present communication, the synthesis of 5-methylxanthyletin and its derivatives is reported.

Results and Discussion

The condensation of 1 with 2-methylbuta-1,3-diene in presence of orthophosphoric acid gave a mixture of four products (A, B, C and D) in the ratio of 3:3:2:10 (overall yield: 70%). The separation of the mixture was achieved by column chromatography on silica gel with petroleum ether.

Compound A (the faster moving fraction) did not give the ferric reaction and its elemental analysis showed the introduction of two isoprene units. The 1H-NMR spectrum of A showed a singlet of one proton at 6.20 ppm (aromatic proton), two singlets at 2.12 (methyl group) and 1.28 (gem. dimethyl groups), a triplet at 2.53 and a multiplet at 1.58-1.87 (each integrating for four protons), assigned to methylene groups. It was thus assigned the structure of 3,4,9,10-tetrahydro-2,2,5,8,8-pentamethyl-2H,8H-benzo[1,2-b:3,4-b']dipyran (2) (non symmetrical structure). Compound B was found to be an isomer of 2. It was identified as 3,4,6,7-tetrahydro-2,2,5,8,8-pentamethyl-2H,8H-benzo[1,2-b:5,4-b']dipyran (3) on the basis of its elemental analysis and 1H-NMR spectral data which showed two distinct triplets at 1.75 and 2.55 (each integrating for four protons, characteristic for chroman methylene groups) along with other usual signals.

Compounds C and D did not give ferric reaction and were found to be isomeric monochromans (elemental analysis). The 1H-NMR spectra of C showed besides other signals two singlets of one aromatic proton each at 6.10 and 6.20 whereas that of D showed two singlets at 6.13 and 6.21. Hence, a clear distinction between the structures of compounds C and D were not possible and either of the compounds could be assigned the structure of 3,4-dihydro-5-hydroxy-2,2,7-trimethyl-2H-1-benzopyran (4) or 3,4-dihydro-7-hydroxy-2,2,5-trimethyl-2H-1-benzopyran (5). The structures of compounds C and D were confirmed as 4 and 5 by further reaction with 2-methylbuta-1,3-