

## A CONVENIENT SYNTHESIS OF ACETYLCROMANS

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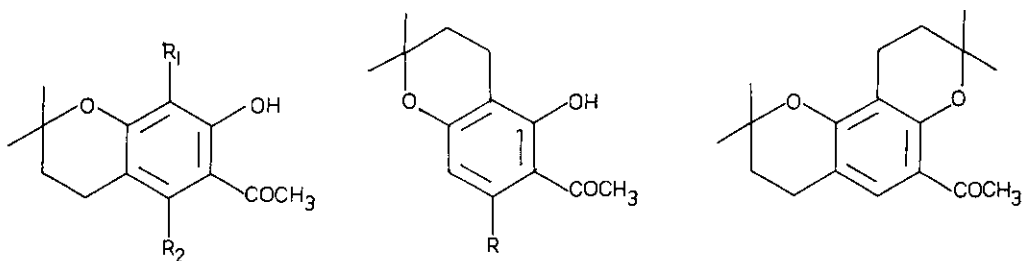
**Abstract** - A convenient one-step synthesis of acetylsubstituted 2,2-dimethylchromans involving the condensation of polyhydroxyacetophenones with 2-methylbut-3-ene-2-ol in presence of orthophosphoric acid is described.

The utility of 2,2-dimethylchromans bearing an acetyl function has been shown for the synthesis of a number of naturally occurring acetylchromenes<sup>1,2</sup>. Such chromans and chromenes are also useful starting materials for the synthesis of many other aromatic hemiterpenes<sup>3,4</sup>. Earlier methods for synthesis of chromans involve the use of Grignard reagent<sup>5</sup> on coumarins or Clemmensen reduction<sup>6</sup> of chromanones. These methods are not suitable for the synthesis of acetylchromans. One attempt to synthesize acetylchromans by the condensation<sup>7</sup> of 2-methylbut-3-ene-2-ol with polyhydroxyacetophenones in presence of 5% citric acid (aq.) resulted in a mixture of products from which acetylchromans could be isolated only in very poor yield (3-6%). In the past such acetylchromans have been obtained by Friedel-Crafts type reaction on the hydroxychromans<sup>8,9</sup> or by acid-catalysed cyclisation of the corresponding o-hydroxyprenyl compounds<sup>10</sup> which themselves are difficult to prepare. Recently a novel method for synthesis of such chromans have been reported from our laboratory, which involves the direct condensation of polyhydroxyacetophenones with isoprene<sup>1</sup>.

During the course of our work on the synthesis of precocenes, acetylchromenes and related compounds, we have been able to develop another convenient and one-step synthesis of acetylchromans (yield, 60-80%). The reaction involves the condensation of 2-methylbut-3-ene-2-ol with polyhydroxyacetophenones in presence of orthophosphoric acid.

The typical experimental procedure consists in the addition of 2-methylbut-3-ene-2-ol (0.8 ml) in petroleum ether (b.p.60-80°; 5 ml) to a well stirred suspension of 2,3,4-trihydroxyacetophenone (1 g), orthophosphoric acid (85%, 1 ml) and petroleum ether (5 ml) during 8 hr at 40°C and stirring continued for further 12 hr. The mixture was neutralized with sodium bicarbonate and extracted with ether. The ethereal extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and distilled. The crude product, thus obtained, was crystallised from benzene - petroleum ether to give a colourless crystalline

compound (1.1 g), m.p.123-124<sup>o</sup>, which was assigned the structure 6-acetyl-7,8-dihydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (1) on the basis of its NMR and direct comparison (m.p., mixed m.p. and superimposed IR) with an authentic sample<sup>1</sup>.



1, R<sub>1</sub> = OH, R<sub>2</sub> = H

2, R = H

4

3, R<sub>1</sub> = R<sub>2</sub> = H

5, R = OCH<sub>3</sub>

6, R<sub>1</sub> = H; R<sub>2</sub> = OCH<sub>3</sub>

2,4-Dihydroxyacetophenone on similar condensation gave 6-acetyl-5-hydroxy-2,2-dimethyl-2H-1-benzopyran (2), m.p.69-70<sup>o</sup>, 6-acetyl-7-hydroxy-2,2-dimethyl-2H-1-benzopyran (3) m.p.118-119<sup>o</sup> and 6-acetyl-2,2,8,8-tetramethyl-3,4,9,10-tetrahydro-2H, 8H-benzo [1,2-b:3,4-b'] dipyrans (4), m.p.78-79<sup>o</sup>, in the ratio of 2:2:1 (overall yield, 70%) respectively. Similarly 2,4-dihydroxy-6-methoxyacetophenone gave 6-acetyl-5-hydroxy-7-methoxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (5), m.p.92-93<sup>o</sup> and 6-acetyl-7-hydroxy-5-methoxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (6), m.p.52-53<sup>o</sup>, in the ratio of 1:1 (overall yield 60%) respectively. All the above products were separated by column chromatography over silica gel and structures given on the basis of <sup>1</sup>H NMR spectral data and direct comparison (m.p., mixed m.p. and superimposed IR) with the authentic samples<sup>1</sup>. The yields obtained are comparable to those obtained in the reaction of isoprene with polyhydroxyacetophenones<sup>1</sup>.

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