

A CONVENIENT ROUTE FOR THE SYNTHESIS OF 3-ALKENYLCOUMARINS
AND CHROMONES

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In view of recent occurrence of 3-alkenylcoumarins and 3-alkenyl-2-methoxychromones, it was considered of interest to devise a convenient route for their synthesis. Though a number of methods are available for the synthesis of 3-alkylcoumarins and chromones, but no method is available for the synthesis of 3-alkenylcoumarins and 3-alkenyl-2-methoxychromones. A convenient route has now been developed for the synthesis of such system. The method involves the use of 3-alkenyl-4-hydroxycoumarin derivatives and then removal of 4-hydroxyl group by tosylation followed by reductive detosylation by Zn-HCl. Further the intermediates 3-alkenyl-4-hydroxycoumarins are known to possess anticoagulant activity and are essential intermediates for the synthesis of naturally occurring 2-substituted furanocoumarins and unsubstituted furanocoumarins which are also known for their physiological activity.

Using the above route the synthesis of 3-allylcoumarin and 3-allyl-2-methoxychromone derivatives has been carried out. The intermediates 3-allyl-4-hydroxycoumarins could not be obtained by the simple Claisen migration of 4-allyloxycoumarins under reduced pressure or in the dimethylaniline, but results in the formation of cyclic structure. In the present method

the intermediates are obtained in very good yield by the controlled Claisen migration of 4-allyloxycoumarins in acetic anhydride in presence of sodium acetate followed by hydrolysis.

Thus, 3-allyl-, 3-allyl-7-methoxy- and 3-allyl-7,8-dimethoxycoumarins have been synthesised by tosylation of appropriate 3-allyl-4-hydroxycoumarins followed by reductive detosylation.

Further the existence of coumarin-chromone tautomerism in 4-hydroxycoumarins prompted us to observe such tautomerism in 3-allyl-4-hydroxycoumarins. Thus, methylation of 3-allyl-4-hydroxycoumarins were carried out with diazomethane in ether, which resulted in the formation of 1:1 mixture of the corresponding 3-allyl-4-methoxycoumarin and 3-allyl-2-methoxychromone. This indicates that such tautomerism also exists in 3-allyl-4-hydroxycoumarins.