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A NEW ROUTE TO THE SYNTHESIS OF 3-METHYLENECOUMARINS-VIA LEWIS ACID CATALYZED REARRANGEMENT OF METHYL α-ARYLOXYMETHYLACRYLATES

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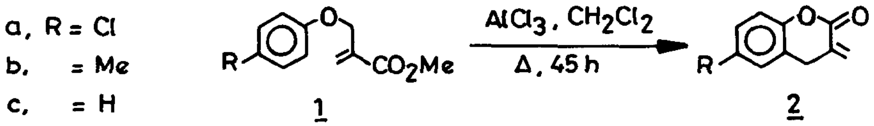
Summary: Methyl-α-aryloxymethylacrylates 1a-c have been found to rearrange to furnish the methylenecoumarins 2a-c when refluxed in methylene chloride in the presence of anhydrous $AlCl_3$.

Several synthetic strategies have been developed in recent times towards the formation of α-methylene γ- and δ-lactones[1,2]. However, there appears to be only a couple of reports regarding the synthesis of 3-methylenecoumarins that too by circuitous routes[3,4].

We wish to report in this paper an elegant synthesis of 3-methylenecoumarins 2 by the Lewis acid catalyzed Claisen rearrangement of methyl α-aryl oxymethylacrylates 1. Refluxing the ester 1a[5](.005 mol) in the presence of anhydrous $AlCl_3$(.01 mol) in 100 ml of CH_2Cl_2 for 45 h followed by work up furnished the methylenecoumarin 2a in 80% yield as a solid melting at 120-122°C IR($CHCl_3$): 1755 cm^{-1}(C=O); UV(EtOH): 231(log ε 3.37),259(log ε 3.21),278(log ε 3.01); NMR($CDCl_3$/TMS) δ-values: 3.8(t,2H, benzylic protons), 5.7 & 6.4(t,2H, exomethylene protons) and 6.9-7.3(m,3H, ArH); MS m/z 194(M^+). NMR spectrum of the crude reaction product showed the formation of only methylenecoumarin and not the 3-methylcoumarin, a product that could arise by isomerisation. Two other esters 1b and 1c were found to rearrange similiarly furnishing the corresponding methylenecoumarins 2b and 2c respectively. (Table I)

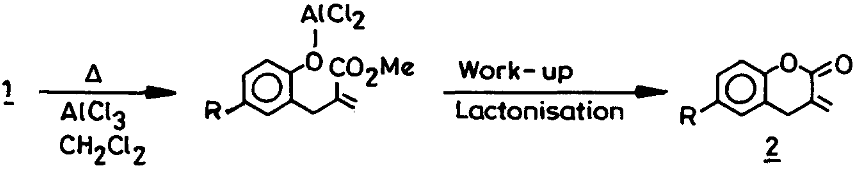
TABLE - I

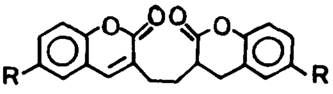


Starting Ester	Product	Yield	M.Pt in °C
1a	2a	80%	120-122
1b	2b	76%	78 - 80
1c	2c	65%	66 - 68

The rearrangement of the ester 1a in the presence of other Lewis acids like BF_3-Et_2O, $SnCl_4$, $TiCl_4$ and $ZnCl_2$ in diffrent solvents like CH_2Cl_2, $CHCl_3$ CCl_4 and hexane were studied. However, the best combination appeared to be anhydrous $AlCl_3$ in methylene chloride. Interestingly, the ester 1a failed to rearrange in refluxing trifluoroacetic acid (45 h). The starting ester was recovered unchanged. The same methylenecoumarin 2 was observed to be formed by the thermal rearrangement of α-aryloxymethylacrylic acid in a large volume of o-dichlorobenzene[6].

Lewis acid catalyzed Claisen rearrangement is fairly well documented[7]. The formation of the methylenecoumarin 2 can be rationalised as in the following scheme. The rearrangement was also found to give a small amount of the dimer 3 presumably formed by an Ene reaction indicating the high reactivity of the methylenecoumarin.





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The high yields and simplicity of this rearrangement are very attractive factors of the present study. The potentials of the methylenecoumarins to serve as synthons for further elaboration and manipulation are being investigated.

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