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TRIFLUOROACETIC ACID CATALYZED AND THERMAL REARRANGEMENT OF α - ARYLOXYMETHYL CINNAMIC ACIDS.

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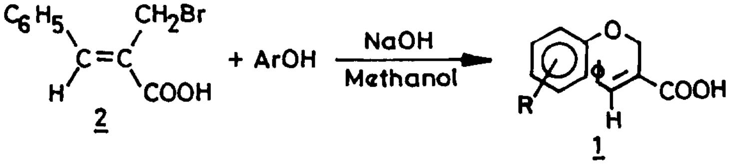
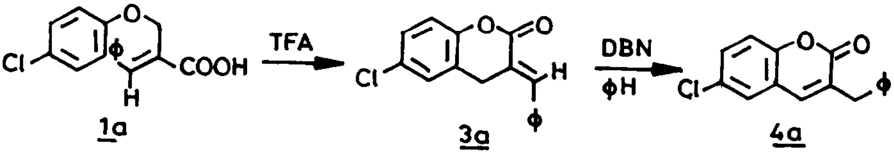
Abstract. Several α - aryloxymethyl cinnamic acids 1 have been rearranged in refluxing trifluoroacetic acid (TFA). The thermal rearrangement of the same acids in Polyethylene glycol - 200 (PEG - 200) has also been investigated.

The use of TFA as a solvent in ortho Claisen rearrangement has been reported to cause tremendous rate enhancement (as much as 10^5) as compared to that in other solvents (1,2). An interesting synthesis of a naturally occuring isocoumarin ± Mellin has been reported via an ortho Claisen rearrangement in TFA (3). In this paper, we report the TFA catalyzed rearrangement of several α - aryloxymethyl cinnamic acids 1. These acids were prepared by the reaction of phenols with α - bromomethyl cinnamic acid 2 (4) in the presence of sodium hydroxide.



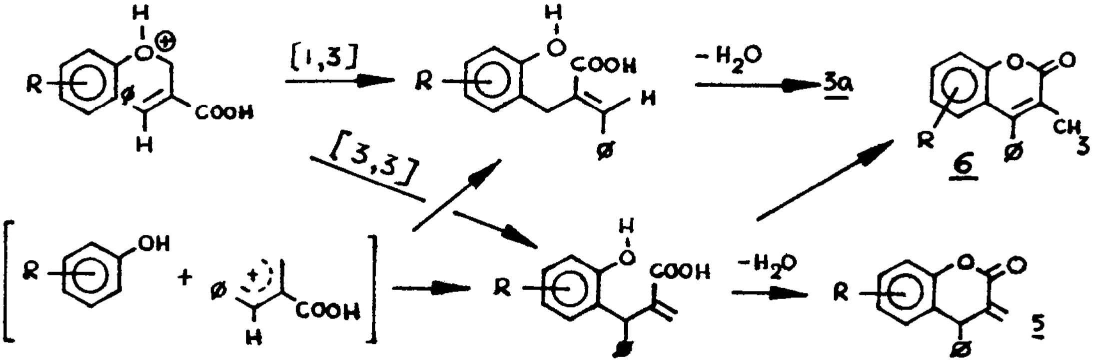
There was no reaction when α- aryloxymethylacrylic acids (5) or their methyl esters were refluxed in TFA for 24 hr or even for longer periods. However, refluxing α-p- (chlorophenoxymethyl) cinnamic acid 1a in a ten-fold excess of TFA for 24 hr followed by workup furnished a neutral product in 80% yield ; m.p. 158-159°C. IR (KBr) spectrum showed a carbonyl absorption at 1700 cm^{-1}. The PMR ($CDCl_3$/TMS) showed the following features ; δ 4.0 (d, 2H, J = 3 Hz), 6.9-7.2 (m, 3H), 7.4 (s, 5H) and 8.1 (t, 1H, J = 3 Hz). Mass spectrum and elemental analysis indicated a molecular formula of $C_{16}H_{11}ClO_2$. Based on these data, structure 3a was assigned for the product obtained in the rearrangement. The absence of any fragment corresponding to m/e - 91 ($C_6H_5CH_2^+$) in the mass spectrum ruled out the alternative structure 4a. The more favourable 'E' configuration about the double bond is assumed. In the case of other acids, viz., p-methyl 1b, p-ethyl 1c and 3,5-dimethyl 1d, the products were found to be a mixture of 3-benzylidene coumarins 3 and 3-methylene - 4 - phenyl coumarins 5 (6), as evidenced by PMR spectrum of the crude reaction mixture. A clean separation of the products could not be achieved. The coumarin 3a was smoothly isomerized to the 3-benzyl coumarin 4a (m.p. 140-142°C) with DBN in refluxing benzene for 2 hr. The PMR spectrum of the isomerized product showed significantly the absence of the downfield triplet at δ 8.1. The methyl esters of the acids 1 were also found to behave similarly when refluxed in TFA. The same coumarin 3a was obtained when the



acid 1a was refluxed in o-dichlorobenzene in the presence of p-toluene sulfonic acid.

In remarkable contrast to the TFA catalyzed rearrangements, the thermal rearrangements of these acids 1 in high boiling solvents afforded only the products arising via a (3,3) sigmatropic rearrangement. Further, it was observed that the nature of the solvent employed, played a significant role in determining the nature of the final product. Thus refluxing the acids 1a and 1b in o-dichlorobenzene for 22 hr gave rise to the respective 3 - methylene - 4 - phenyl coumarins 5a (m.p. 123-125°C, 50%) and 5b (m.p. 105-106°C, 54%), whereas in PEG - 200 (reflux temperature for 1 hr), a solvent which has come to prominence in recent times (7,8,9), or in N,N - diethylaniline (reflux temperature for 3 hr) the 3-methyl-4-phenyl coumarins 6a and 6b were the exclusive products. A few other cinnamic acids also underwent this rearrangement.

The TFA catalyzed rearrangement may essentially proceed by a concerted (1,3) and (3,3) sigmatropic rearrangements to furnish the coumarins 3a and 5 respectively. Alternatively, a non-concerted as well as a concerted mechanism may operate simultaneously. These two possible modes of rearrangement are depicted in the Chart. Under thermal conditions, a (3,3) sigmatropic rearrangement is likely to be the sole pathway leading to the methylene coumarins 5 or methyl coumarins 6. The mechanistic implications of these transformations are being investigated.



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All the isolated compounds reported in this paper showed satisfactory elemental analysis and spectral properties.

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