An Apparent Similarity between the Mass Spectral and Thermal Reactions of *trans*-Pentafluorocinnamic Acid. Synthesis of 5,6,7,8-Tetrafluorocoumarin

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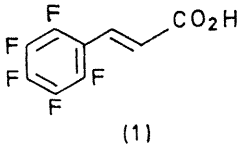
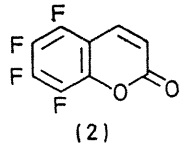
Summary The pyrolysis of *trans*-pentafluorocinnamic acid at 400° or the photolysis of sodium pentafluorocinnamate at 100° afford 5,6,7,8-tetrafluorocoumarin.

INTEREST has been shown in recent years in apparent similarities between high-energy mass spectral, thermal, and photochemical processes,[1] and in intramolecular nucleophilic cyclisation reactions.[2]



(1)



(2)

The first step in the mass spectral fragmentation of *trans*-cinnamic acid involves the loss of the hydroxyl radical.[3] We now report that the first step in the fragmentation of the molecular ion of pentafluorocinnamic acid[4] (**1**) involves (as the major course) the loss of hydrogen fluoride.† Thereafter the fragmentation shows a similarity to the reported[5] mass spectrum of coumarin.

The isomerisation of *trans*-cinnamic acid and derivatives to a mixture of the *cis*- and *trans*-isomers can be achieved thermally, and photochemically in solution,[6] and could be achieved easily in the mass spectrometer in the case of the compound (**1**). In accord with expectation we have prepared 5,6,7,8-tetrafluorocoumarin (**2**) both thermally and by a combined photochemical and thermal method. When the compound (**1**) was heated *in vacuo* at 400° for 4 h we obtained compound (**2**)‡ in 84% yield. Sodium *trans*-pentafluorocinnamate was converted partially into the *cis*-isomer when irradiation was carried out (Hanovia, medium-pressure source) in aqueous solution at room temperature. However, when the isomerisation was carried out at 100° the compound (**2**) steam distilled from the reaction mixture and was isolated in 48% yield.

We thank The Imperial Smelting Corporation for a grant (to A. P. P.) and for supplies of pentafluorobenzaldehyde. We also thank the P.C.M.U. (Aldermaston) and the S.R.C. for mass spectral measurements.

(*Received, May 17th*, 1971; *Com.* 774.)

† The mass spectral fragmentations reported are supported by accurate mass measurements and by the observation of the appropriate metastable peaks.

‡ Satisfactory analytical and spectral data were obtained for this compound.

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