Reaction of Phosphorus Pentachloride with β-Ketoesters. A Convenient Route for the Preparation of β-Chlorovinyl Acids

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Summary A number of *trans*-β-chlorocinnamic acids have been synthesised by the action of phosphorus pentachloride on the corresponding β-ketoesters.

From our interest in the kinetics and mechanisms of alcoholysis of chloro-olefins,[1] we wanted to prepare compounds of the type $R^1C_6H_4{\cdot}CCl{=}CH{\cdot}CO_2R^2$. Earlier preparations of β-chlorocinnamic acid from phenylacetylene and oxalyl chloride,[2] or by the reaction of PCl_5 with benzyl acetic ester,[3] reported low yields (16 and 25% respectively) and a mixture of *cis–trans*-isomers. The reaction of phosphorus pentachloride with β-ketoesters, readily prepared by acylation of ethyl acetoacetate with the appropriate acid chloride,[4] was investigated as a possible route to β-chlorovinyl acids.

Treatment of (Ia—d) with PCl_5 in benzene gave directly the corresponding β-chlorovinyl acids (IIa—d) (40—50%).

p-$R{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (I) p-$R{\cdot}C_6H_4{\cdot}CCl{=}CH{\cdot}CO_2H$ (II)

a; R = H, b; R = Me, c; R = NO_2, d; R = Cl.

The existence of *cis*- and *trans*-(IIa), was indicated by the two vinylic proton peaks in the n.m.r. spectrum in regions similar to those reported[5] for ethyl β-chloro-*cis*- and -*trans*-crotonates. Pure *trans*-(IIa) only was obtained by fractional crystallisation of the barium salt of the crude acid. The β-ketoesters (Ib—d), however, gave only the *trans*-isomers (IIb—d) as shown by n.m.r. spectra and attempted fractional crystallisations of their barium salts. Compounds (IIb—d) are new and their elemental analysis, and i.r. and n.m.r. spectra are in complete agreement with the assigned structures. The n.m.r. absorptions of the vinylic protons in methyl α-chlorocinnamates[6] appear at low fields (indistinguishable from the phenyl protons) as compared to those found here for the β-chloro-isomers.

The isolation of only the *trans*-isomers, presumably, favours a mechanism in which PCl_4^+–PCl_6^- ions react with the keto-group of the ester as with ketones,[7] rather than with the enol-form. This will be discussed in detail in the full paper.

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