Treatment of Cinnamic Acids with Polyphosphoric Acid

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Summary Polyphosphoric acid has been found to isomerize *cis-p*-methoxycinnamic acid to *trans-p*-methoxycinnamic acid and to cleave a benzyl ether; however, there is no evidence for the previously reported *trans*- to *cis*-isomerization of cinnamic acids.

As part of our synthetic studies on the *Lythraceae* alkaloids[1] we required some substituted *cis*-cinnamic acids [*e.g.*, the *cis*-4-benzyloxy-3-bromo derivative (**1**)]. Recently, Rao and Filler reported the 'nearly quantitative' isomerization of several *trans*-cinnamic acids to their *cis*-isomers by the action of polyphosphoric acid (PPA).[2] The simplicity of this contrathermodynamic[3] isomerization encouraged us to apply it to the preparation of more complex *cis*-cinnamic acids.

Thus, *trans*-4-benzyloxy-3-bromocinnamic acid was treated with PPA[4] on a steam bath for 90 min, then crushed ice was added as described.[2] A 70% yield of *trans*-3-bromo-4-hydroxycinnamic acid was isolated but none of the desired *cis*-4-benzyloxy-3-bromocinnamic acid (**1**) or *cis*-3-bromo-4-hydroxycinnamic acid could be detected by n.m.r. spectroscopy. The cleavage of the benzyl group was not surprising;[5] however, the lack of evidence for isomerization was of concern. The PPA treatment was then repeated on the simpler *trans*-cinnamic, -*p*-chlorocinnamic, -*p*-methoxycinnamic (**2**), and -3-bromo-4-hydroxycinnamic acids, the first three of which had been included in Rao and Filler's original study. The material recovered (usually $>90\%$) contained only the *trans*-cinnamic acids as determined by m.p.s and n.m.r. spectroscopy. Similar results were obtained when commercial PPA was used,[6] when reactions were conducted at room temperature for long periods, or when smaller substrate: PPA ratios were employed.

As a further test of the previous results, the fate of *cis-p*-methoxycinnamic acid (**3**) in PPA was investigated. Isomerization to the *trans*-compound (**2**) is rapid in aqueous sulphuric acid.[3] However, if the results of ref. 2 are correct (**3**) should be recovered unchanged from PPA treatment. Thus (**3**), m.p. 64—65 °C (lit.,[7] 67—68 °C), prepared from *cis-p*-hydroxycinnamic acid by treatment with dimethyl sulphate in aqueous sodium hydroxide, was treated with PPA as above. The *trans*-compound (**2**) was isolated in 90% yield, m.p. 170—172 °C (lit.,[7] 174 °C).[7] The n.m.r. spectrum of (**2**) has a one-proton doublet (J 16 Hz) at δ 6·30 whereas (**3**) showed a doublet (J 13 Hz) at δ 5·80 as expected.[7]

Only one other acid-catalysed, contrathermodynamic isomerization of a cinnamic acid has been reported. In this case, *trans-o*-chlorocinnamic acid was isomerized to the *cis*-isomer in low yield by the action of aluminium chloride.[8] In the light of the results reported here, these reported isomerizations should be considered with caution.

We have not investigated the generality of the PPA cleavage of benzyl ethers. However, there appears to be no advantage over the more common reagents for this purpose.[5]

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