

***trans*- to *cis*-Isomerisation of Cinnamic Acids and Related Carbonyl Compounds**

By Y. SHYAMSUNDER RAO*

(Department of Chemistry, Kennedy-King College, Chicago, Illinois 60621)

and ROBERT FILLER*

(Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616)

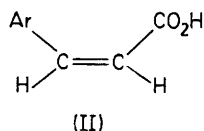
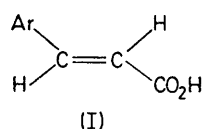
Summary Polyphosphoric acid converts *trans*-cinnamic acid and *trans*-benzylidenacetophenone into their *cis*-isomers and *trans,trans*-5-phenylpenta-2,4-dienoic acid into the *trans,cis*-isomer.

THE conversion of *trans*-cinnamic acid (I, Ar=Ph) into its *cis*-isomer (II) is usually achieved by chemical means, *viz.*, preparation of the dibromohydrocinnamic acid, alkaline dehydrobromination, and catalytic reduction of the resulting phenylpropionic acid.¹ Under photochemical conditions, (I) undergoes 2 + 2 cycloaddition to give α -truxillic acid.

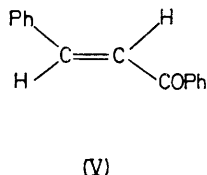
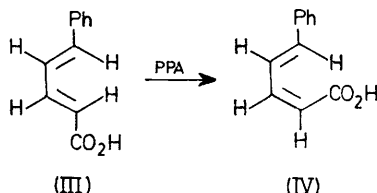
The *cis*-isomer (II) has reportedly been isolated by u.v. irradiation of (I) in 2% acetic acid on powdered wood.²

Recently we described the use of polyphosphoric acid (PPA) to effect the conversion of the *Z*- into the *E*-isomer in 4-arylidene-5(4*H*)-oxazolones.³ In extending the scope of this unusual transformation, we now report the ready *trans*- to *cis*-isomerisation of cinnamic acids and related carbonyl compounds. This one-step procedure consists of heating (I) in PPA at 80–95 °C for 90 min and pouring the resulting solution over crushed ice to afford a nearly quantitative yield of (II), m.p. 68 °C (from benzene). While

the use of PPA in the synthesis of flavones from *trans*-cinnamic acids has been described,⁴ no mention was made of the probable initial isomerisation, nor was the isolation



(Ar = Ph)



of any *cis*-acid reported. House⁵ has suggested that isomerisation of the carbon-carbon double bond at 100 °C is faster than the subsequent intramolecular acylation to form the cyclised product. Under our reaction conditions, we have succeeded in intercepting and isolating the *cis*-isomer.

This procedure was also employed for the preparation of *cis*-isomers of three substituted cinnamic acids (I, Ar = 4-MeOC₆H₄, 4-MeC₆H₄, and 4-ClC₆H₄).⁶ The method is equally effective on an extended conjugated system, *e.g.*, the conversion of *trans,trans*-5-phenylpenta-2,4-dienoic acid (III), m.p. 165 °C, into the *trans-cis*-isomer (IV), m.p. 138 °C. Moreover, *trans*-benzylidenacetophenone (V) is easily converted into its much less accessible *cis*-isomer.⁷

Preliminary mechanistic studies indicate that crotonic and fumaric acids and *trans-trans*-1,4-diphenylbuta-1,3-diene are not isomerised in PPA. It appears, therefore, that the presence of both a carbonyl function and an aryl group is essential.

(Received, 26th March 1976; Com. 317.)

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² P. Comte, G. Zwingelstein, A. Ville, and C. Mentzer, *Compt. rend.*, 1957, **245**, 1144.

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⁴ N. Hasebe, *Nippon Kagaku Zasshi*, 1961, **82**, 1728; 1962, **83**, 222; 1968, **89**, 534; N. Hasebe and A. Omura, *ibid.*, p. 99.

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⁶ I. M. Heilbron, 'Dictionary of Organic Compounds,' Oxford University Press, New York, 1965.

⁷ R. E. Lutz and R. H. Jordan, *J. Amer. Chem. Soc.*, 1950, **72**, 4090; H. H. Szmant and A. J. Basso, *ibid.*, 1952, **74**, 4397.