

Direct Chlorodecarboxylation of the *trans*-Cinnamate Ion

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BROMODECARBOXYLATION of aromatic carboxylic acids, especially of hydroxy-, amino- and alkoxybenzoic acids, is well established.¹ We describe here evidence for the direct electrophilic displacement of carbon dioxide from the *trans*-cinnamate ion by chlorine in acetic acid.

The chlorination of *trans*-cinnamic acid (0.05M) in acetic acid gives rise to four addition products, *erythro*- and *threo*- $\alpha\beta$ -dichloro- and *erythro*- and *threo*- β -acetoxy- α -chloro- β -phenylpropionic acid. This product mixture (0.05M) is unchanged when left for 4 hours in acetic acid containing 0.1M-lithium acetate and an excess of chlorine. However, chlorination of *trans*-cinnamic acid (0.05M) in acetic acid containing 0.1M-lithium acetate and an excess of chlorine for 4 hours, gave the same

four addition products, in the same ratio, in 90% total yield, together with two new products α -acetoxy- $\beta\beta$ -dichloro- and $\alpha\beta\beta$ -trichloro-ethylbenzene (I and II respectively) in about 10% yield. When the chlorination was carried out in the presence of 1.0M-lithium acetate and an excess of chlorine, the four addition products were formed in only about 40% yield though in the same ratio, and the decarboxylated products (I) and (II) were formed in a total of *ca.* 60% yield.

It is clear that the decarboxylated products (I) and (II) are not formed primarily by the decomposition of the addition products, rather that they are formed by further chlorination of ω -chlorostyrene which is produced during the chlorination process in the more basic media. Moreover, the

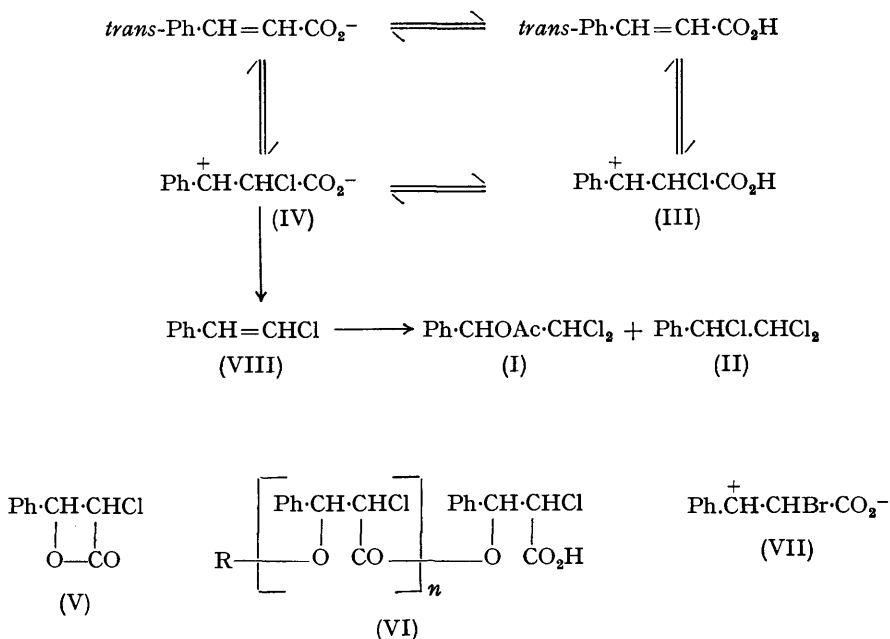
¹ E. Grovenstein and U. V. Henderson, *J. Amer. Chem. Soc.*, 1956, **78**, 569; E. Grovenstein and G. A. Ropp, *J. Amer. Chem. Soc.*, 1956, **78**, 2560.

constancy of the addition product ratio indicates that the mechanism of addition has not been disturbed other than by the diminution of the total number of molecules undergoing addition. The decarboxylation must therefore be the result of either a separate mechanism or a diversion of one of the intermediates in the addition mechanism prior to the product-determining step.

The most likely explanation is that whilst the

(which might have been expected if an unstable β -lactone had been formed)² could be detected in the products, it is likely that the zwitterionic intermediate (IV) has a very short lifetime.

This zwitterionic intermediate is very similar to the zwitterion (VII) proposed as an intermediate in the non-stereospecific loss of bromide ion and carbon dioxide from sodium *erythro*- $\alpha\beta$ -dibromo- β -phenylpropionate in solvating media.^{3,4}



carbonium ion (III) formed from *trans*-cinnamic acid prefers to add chloride ion or acetate ion rather than to lose carbon dioxide, the zwitterionic intermediate (IV) from the *trans*-cinnamate ion loses carbon dioxide, to form ω -chlorostyrene (VIII), much more readily than it adds chloride or acetate ions. Because the exact proportions of the *trans*-cinnamate ion and *trans*-cinnamic acid in acetic acid/lithium acetate solutions are uncertain, it is not possible to say whether the zwitterionic intermediate (IV) is formed directly from the *trans*-cinnamate ion or by ionisation of the carbonium ion (III). However, since no β -lactone (V) nor the polymeric product (VI)

An excess of chlorine was used in all the experiments in order to ensure complete chlorination of the ω -chlorostyrene to (I) and (II). This was because it was found that the ω -chlorostyrene was partially chlorinated to (I) and (II) even when only one equivalent of chlorine was used, thereby complicating the product mixtures and making their estimation more difficult. The products were analysed by a combination of proton magnetic resonance spectra and elemental analyses both before and after separation by chromatography.

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² T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Amer. Chem. Soc.*, 1948, **70**, 998.

³ S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, 1953, **75**, 2645.

⁴ E. Grovenstein and D. E. Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 2639.