499. *Studies in Pyrolysis. Part XIX.*[1] *Competition between Intra-acyl Scission and Decarboxylation in the Pyrolysis of Aryl Esters of αβ-Unsaturated Carboxylic Acids.*

By P. E. Reininger, P. D. Ritchie, and (in part) D. Ferguson.

Phenyl cinnamate, at *ca.* 500°, and phenyl cyclohex-1-enecarboxylate, at *ca.* 600°, both undergo two competitive pyrolytic scissions: (i) intra-acyl scission to a labile alkyne and phenyl formate (followed by secondary scissions) and (ii) decarboxylation, the former reaction predominating.

There is some evidence that decarboxylation proceeds by a dual mechanism, but the greatly preponderating mechanism is thought to be concerted and intramolecular.

Until a few years ago, the thermal decarboxylation of carboxylic esters was exemplified almost solely by early observations that various aryl cinnamates,[2,3] maleates,[4] and fumarates[3-5] lose carbon dioxide on slow distillation, with formation of a *trans*-stilbene. The maleates and fumarates break down by two successive decarboxylations, through an aryl β-arylacrylate (*e.g.*, phenyl cinnamate) which sometimes partially survives[5] in the pyrolysate, thus:

$$\underset{\textit{cis or trans}}{\mathrm{ArO_2C{\cdot}CH{:}CH{\cdot}CO_2Ar}} \xrightarrow[-\mathrm{CO_2}]{C^2} \mathrm{Ar{\cdot}CH{:}CH{\cdot}CO_2Ar} \xrightarrow[-\mathrm{CO_2}]{C^2} \underset{\textit{trans}}{\mathrm{Ar{\cdot}CH{:}CH{\cdot}Ar}}$$

It is now realised[6] that decarboxylation (C^2 scission) of esters is relatively common. It competes strongly and generally in the complex breakdown of a range of esters $R{\cdot}CO_2R'$ where R and/or R′ show olefinic or benzenoid unsaturation. For example, phenyl acrylate and methacrylate break down[6] (vapour phase: *ca.* 550°) by a complex route which,

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[1] Part XVIII, Reininger and Ritchie, preceding paper.
[2] Anschütz, *Ber.*, 1885, **18**, 1945.
[3] Anschütz, *Ber.*, 1927, **60**, 1320.
[4] Bischoff and von Hedenström, *Ber.*, 1902, **35**, 4084.
[5] Anschütz and Wirtz, *Ber.*, 1885, **18**, 1947.
[6] Mackinnon and Ritchie, *J.*, 1957, 2564.

simplified by the omission of one or two very minor reactions, is a competition between a major intra-acyl scission to alkyne and transient phenyl formate (the latter undergoing secondary breakdown to carbon monoxide and phenol) and a subordinate but still important decarboxylation.

No other examples of this novel intra-acyl scission have so far been recorded: but it seemed likely, by structural analogy, that it must also have competed in the pyrolysis of aryl cinnamates and fumarates, although the earlier work on these compounds had revealed no primary reaction other than C^2 scission. The pyrolysis of some aryl esters of αβ-unsaturated acids has therefore been more closely studied.

Competitive Primary Routes.—Phenyl cinnamate (I; R = Ph, R′ = H) exhibits the same system of competitive scissions in the vapour phase (*ca.* 500°) as phenyl acrylate[6] (I; R = R′ = H) and methacrylate[6] (I; R = H, R′ = Me), as shown. Secondary products from the cinnamate are phenol, and traces of biphenyl, bibenzyl, and anthracene; the gaseous portion of the pyrolysate consists mainly of carbon monoxide and dioxide, with a little unsaturated hydrocarbon.

		R: R′:	H H	H Me	Ph H
$R{\cdot}CH{:}CR'{\cdot}CO_2Ph$ (I)	$\xrightarrow{E^*}$	$R{\cdot}C{\vdots}C{\cdot}R' + [H{\cdot}CO_2Ph]$	*ca.* 54%	*ca.* 52%	*ca.* 44%
	$\xrightarrow{C^2}$	$CO_2 + R{\cdot}CH{:}CR'Ph$	*ca.* 13	*ca.* 19	*ca.* 34
	$\rightarrow$	Tars (uncharacterised)	*ca.* 29	*ca.* 23	*ca.* 21
		Other minor products	*ca.* 4	*ca.* 6	*ca.* 1

* Here and below, the intra-acyl scission is denoted by the symbol *E*, an extension of the *A*, *B*, *C*, *D* notation for other modes of ester-scission.

Phenol and carbon monoxide are again the known secondary breakdown products[6] of phenyl formate from the *E* scission: but the phenylacetylene which should accompany them in equimolar amount is, in fact, found in much smaller quantity (cf. the similar deficiency of alkyne in the pyrolysis of phenyl acrylate and methacrylate[6]). Presumably the reactive alkyne undergoes secondary reactions and polymerisation, with tar formation. The observed anthracene also possibly arises from phenylacetylene: biphenyl can formally be accounted for by various free-radical reactions: and a separate pyrolysis of *trans*-stilbene, under the same conditions, showed that this substance is the precursor of the surprising product bibenzyl. The stilbene is very stable, and forms little or no tar; but the small amount of decomposed pyrolysand (*ca.* 8%) contains bibenzyl, presumably formed by abstraction of hydrogen from the small amount of tar.

A similar competition between *E* and C^2 scission also occurs when the double bond in the unsaturated acyl group forms part of an alicyclic instead of an open-chain system. It is known[7] that cyclohex-1-enyl benzoate breaks down thermally by a complex competition which includes decarboxylation, although the foregoing type of intra-acyl scission is here structually precluded: but the isomeric ester phenyl cyclohex-1-enecarboxylate (II) undergoes both *E* and C^2 scission. At *ca.* 600°, in a flow-reactor, some 53% survives unchanged; and the constituents of the decomposed fraction are best represented by the annexed reaction scheme. The non-gaseous portion of the pyrolysate consists mainly of recovered ester (II), phenol (from secondary breakdown of phenyl formate), and 1-phenylcyclohexene. There are also two minor unidentified products, possibly derived from the transient intermediate alkyne (cyclohexyne) which should formally accompany the phenyl formate. This alkyne is incapable of stable free existence, and its precise fate is here unknown (cf. its failure to survive in the A^2 scission of cyclohex-1-enyl benzoate[7]). Rather surprisingly, very little tar is formed from ester (II).

Mechanism of Decarboxylation.—It is possible[6] to inhibit the *E* scission of phenyl

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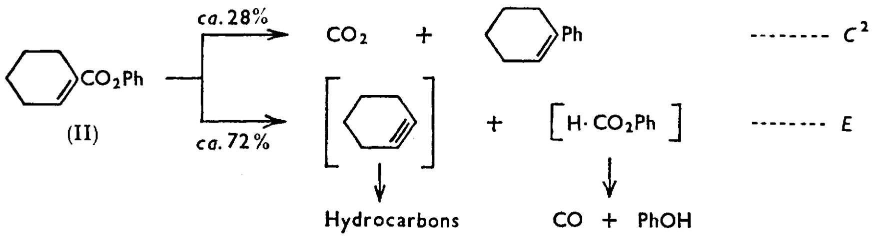
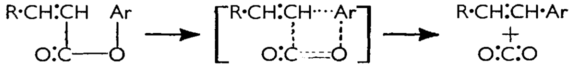
[7] Allan, McGee, and Ritchie, *J.*, 1957, 4700.

acrylate and methacrylate by adding a little quinol to the pyrolysand, without affecting the C^2 scission, which suggests that the latter reaction is not free-radical in character. This view is now confirmed by the copyrolysis of an equimolar mixture of phenyl fumarate and 4-chlorophenyl maleate. Pyrolysed separately, these esters yield *trans*-stilbene and *trans*-4,4'-dichlorostilbene, respectively: but, if the double C^2 scission occurs by a mechanism in which each CO•O group is completely detached from its flanking groups before recombination of the latter (*e.g.*, by a free-radical mechanism), it would be expected that a good deal of the unsymmetrical 4-chlorostilbene would be formed by pairing of unlike aryl radicals. Copyrolysis in a flow-reactor at *ca.* 500° led to a major carbonisation; but a much cleaner pyrolysate was obtained in a static reactor at *ca.* 340° (*i.e.*, some 40° above the onset temperature for evolution of carbon dioxide). Under the latter conditions, the non-gaseous portion of the pyrolysate contained phenyl cinnamate (28%), *trans*-4,4'-dichlorostilbene (49%), *trans*-stilbene (22%), and *trans*-4-chlorostilbene (1%). No *p*-chlorophenyl 4-chlorocinnamate was present; and this fact, coupled with the high proportion of dichlorostilbene, indicates that the chlorinated component of the original pyrolysand deomposed more rapidly than its chlorine-free analogue.



The very small yield of mixed (unsymmetrical) stilbene clearly rules out a major homolytic mechanism, at least up to *ca.* 340°. Whether the actual mechanism is molecular or heterolytic is not yet known, and the problem is being studied further; but the present results at least point strongly to a concerted intramolecular mechanism for each C^2 scission, in which bond-breaking and bond-formation operate concurrently by way of some such transition-state as (A).



$$\begin{array}{cc}\mathrm{R{\cdot}CH{:}CH} & \mathrm{Ar}\\ | & |\\ \mathrm{O{:}C} & \!\!-\!\!\!-\mathrm{O}\end{array} \longrightarrow \left[\begin{array}{cc}\mathrm{R{\cdot}CH{:}CH}\cdots & \mathrm{Ar}\\ \vdots & \vdots\\ \mathrm{O{:}C} & \!\!=\!\!=\mathrm{O}\end{array}\right] \longrightarrow \begin{array}{c}\mathrm{R{\cdot}CH{:}CH{\cdot}Ar}\\ +\\ \mathrm{O{:}C{:}O}\end{array}$$

(A)

This is also consistent with an observation by Filachione *et al.*[8] on the vapour-phase pyrolysis (*ca.* 550°) of certain aryl α-acetoxypropionates. These undergo the predictable A^1 scission to acetic acid and an aryl acrylate ($CH_2{:}CH{\cdot}CO_2Ar$); and, where Ar = *p*-t-butylphenyl, the pyrolysate contains a little *p*-t-butylstyrene, which must have arisen by C^2 scission of the acrylate. This suggests that there is no change of orientation during decarboxylation, and hence (as in the above four-centre transition-state) no complete detachment of the aryl group from its neighbouring atoms at any stage; but it should be emphasised that the *p*-t-butylstyrene was not rigorously identified, nor was a search for its *o*- and *m*-isomers reported.

The presence of a trace of the mixed stilbene raises an interesting question. Very probably, it arises by a minor amount of ester-interchange between the copyrolysands during the rather prolonged heating (90 min.), giving a mixed fumarate and/or maleate as the true precursor of decarboxylation. Nevertheless, the possibility cannot be excluded that C^2 scission occurs by two competing mechanisms—a major intramolecular mechanism, and a minor mechanism of some other type responsible for the trace of mixed stilbene.

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[8] Filachione, Lengel, and Ratchford, *J. Amer. Chem. Soc.*, 1950, **72**, 839.

It is interesting that a duality appears [9] in the analogous decarboxylation of vinyl benzoate (*ca.* 520°), where C^2 scission is predominantly a homogeneous vapour-phase reaction but also occurs, in part, heterogeneously at the reactor wall.

EXPERIMENTAL

General Methods.—The Pyrex flow-reactor and accessories, and the general procedure for flow-pyrolysis, were of the type already described.[6,7]

Analysis of Products.—Pyrolysate components were identified as previously described.[1]

Preparation of Pyrolysands.—*Phenyl cinnamate.* Prepared by Womack and McWhirter's method [10] (74%), the ester had m. p. 75° (lit.,[10] m. p. 75—76°).

Phenyl fumarate. Attempts to prepare phenyl maleate by recorded methods [3,11] were unsuccessful, and the following modified method led, instead, to phenyl fumarate. Phenol (48 g.) and sodium carbonate (27 g.) were dissolved in water (400 ml.), and maleic anhydride (50 g.) was slowly added, with stirring, in an attempt to produce phenyl hydrogen maleate. The product (26 g.) was precipitated by addition of dilute hydrochloric acid and heated at 100° for 1 hr. with thionyl chloride (30 g.). The excess of the latter was removed and the residue heated for 4 hr. with phenol (15 g.): phenyl fumarate separated (17%) when the mixture was cooled, giving crystals, m. p. 162—163°, from toluene–heptane (m. p.[4] of fumarate, 161—162°: m. p.[3] of maleate, 73°). Infrared spectrometry showed the band [12] at *ca.* 970 cm.$^{-1}$ characteristic of the *trans*-configuration.

p-*Chlorophenyl maleate.* A preparation analogous to the foregoing yielded the *ester* as crystals, m. p. 116°, from toluene–heptane (Found: C, 56·6; H, 3·2; Cl, 21·2. $C_{16}H_{10}Cl_2O_4$ requires C, 57·0; H, 3·0; Cl, 21·1%). It is clear that in this instance the product has retained the *cis*-configuration; its infrared spectrum lacks the band [12] at *ca.* 970 cm.$^{-1}$, and its m. p. differs from that recorded [2] for *p*-chlorophenyl fumarate (178°).

Phenyl cyclohex-1-*enecarboxylate.* 1-Cyanocyclohexene was prepared by pyrolysis of the benzoate of cyclohexanone cyanohydrin,[13] and hydrolysed to cyclohex-1-enecarboxylic acid by heating it with acetic acid and 50% sulphuric acid. The acid was converted into its chloride, in 50—60% yield, by treatment with thionyl chloride; and the acid chloride, treated with phenol in pyridine, yielded the *ester* (50—60%) as needles, m. p. 62° [from light petroleum (b. p. 60—80°) or ethanol–water] (Found: C, 77·0; H, 6·7%. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%).

Preparation of Reference Standards for Chromatography and Spectrometry.—The following were prepared by published methods (other necessary standards were obtained commercially): 4-chlorostilbene, m. p. 128° (lit.,[14] m. p. 129°); 4,4′-dichlorostilbene, b. p. 215—230°/10 mm., m. p. 174° (lit.,[15] m. p. 175—176°); phenylacetylene, b. p. 137—139° (lit.,[16] b. p. 137—139°); 1-phenylcyclohexene, b. p. 126—128°/18 mm. (lit.,[17] b. p. 129—130°/20 mm.).

Pyrolysis of Phenyl Cinnamate.—The ester (30 g.), pyrolysed at 500° (feed-rate, 0·35 g./min.; residence time, 153 sec.), yielded 22·0 g. of condensed pyrolysate (*a*) and 2·8 l. of uncondensed gas (*b*). Liquid (*a*) contained suspended solid (3·5 g.), identified as pure *trans*-stilbene (mixed m. p. and gas–liquid chromatography); the filtrate, when distilled, yielded (i) 0·5 g., b. p. 18—50°/1 mm., (ii) 3·5 g., b. p. 50—140°/1 mm., (iii) 8·5 g., b. p. 140—230°/1 mm., and (iv) 6·0 g. of residual tar. Fraction (i) contained toluene, phenylacetylene, phenol, and traces of two unidentified components (minor chromatographic peaks): fraction (ii) contained phenol and *trans*-stilbene: fraction (iii) contained phenol, biphenyl, bibenzyl, *trans*-stilbene, anthracene, unchanged pyrolysate (*ca.* 3 g.), and traces of three unidentified components of fairly high b. p. The gas (*b*) contained carbon monoxide (40%), and dioxide (55%) and unsaturated hydrocarbons (5%).

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[9] Part XXI, Bengough, Ritchie, and Steedman, *J.*, 1963, 2697.
[10] Womack and McWhirter, *Org. Synth.*, 1955, **3**, 714.
[11] Bader and Kontowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 5416.
[12] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 34.
[13] Bennett, Deans, Harris, Ritchie, and Shim, *J.*, 1958, 4508.
[14] Bergmann, Weizman, and Schapiro, *J. Org. Chem.*, 1944, **9**, 408.
[15] Lutz and Murphy, *J. Amer. Chem. Soc.*, 1949, **71**, 478.
[16] Fiesselmann and Sasse, *Ber.*, 1956, **89**, 1775.
[17] Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 1321.

Pyrolysis of trans-*Stilbene.*—Stilbene (10 g.), pyrolysed at 500° (feed-rate, 0·37 g./min.; residence time, 125 sec.), yielded *ca.* 8·0 g. of solid pyrolysate (balance lost as tar, and by hold-up in reactor): there was no gaseous pyrolysate. Gas–liquid chromatography of the total solid pyrolysate showed only two peaks, corresponding to bibenzyl and unchanged pyrolysand. Infrared spectrometry confirmed this; the pyrolysate showed major bands at 905 and 970 cm.$^{-1}$, the former being shown only by a reference specimen of pure bibenzyl and the latter only by a reference specimen of pure *trans*-stilbene (no other products indicated).

Pyrolysis of p-*Chlorophenyl Maleate.*—The onset-temperature for evolution of carbon dioxide, measured by the method described previously,[1] was $T(CO_2) = 305°$.

Copyrolysis of Phenyl Fumarate and p-*Chlorophenyl Maleate.*—Trial runs with an equimolar mixture of the two esters in a flow-reactor at *ca.* 500° led to very heavy carbonisation. A static reactor was then used, consisting of a vertical Pyrex vessel (height 6 in., diam. 1 in.), fitted with a reflux condenser and an inlet tube to admit a carrier-stream of nitrogen. The vessel was heated for 90 min. at *ca.* 340°, *i.e.*, some 35° above $T(CO_2)$ for the chloro-ester. Under these conditions the pyrolysate was not markedly carbonised and consisted (gas–liquid chromatography) of phenyl cinnamate (28%), *trans*-stilbene (22%), *trans*-4,4′-dichlorostilbene (49%), and *trans*-4-chlorostilbene (1%). There were no further peaks in the chromatogram.

Pyrolysis of Phenyl Cyclohex-1-*enecarboxylate.*—A preliminary run at *ca.* 550° produced little breakdown. At *ca.* 600° (flow-reactor) the ester (7 g.) yielded a semi-solid pyrolysate (6 g.) consisting of unchanged pyrolysand (62%), phenol (19%), 1-phenylcyclohexene (12%), and two minor unidentified products (*ca.* 5% and *ca.* 2%) (gas–liquid chromatography). The exit gases contained carbon monoxide and dioxde and hydrocarbons. There was very little tar.

Infrared Spectra.—The infrared absorption spectra of 4-chlorostilbene (D.M.S. Index No. 9925) and 4,4′-dichlorostilbene (D.M.S. Index No. 9926) have been recorded.

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