500. *Studies in Pyrolysis. Part XX.*[1] *Competitive Routes in the Pyrolysis of Some Enol Benzoates.*

By W. M. MUIR and P. D. RITCHIE.

In agreement with previous predictions, isopropenyl and α-phenylvinyl benzoate break down thermally (*ca.* 500°) by three competing primary scissions: major rearrangement to a β-diketone, decarboxylation, and minor alkenyl–oxygen scission. Secondary breakdown of certain primary products also occurs.

A minor reaction (probably B^2 scission) yielding a trace of benzaldehyde competes in the pyrolysis of vinyl benzoate at *ca.* 500°.

THE thermal vapour-phase rearrangement of various enol carboxylates to β-diketones [2,3] has been shown to be accompanied by various minor competitive scissions.[3,4] The results have been applied to interpret the pyrolysis of vinyl benzoate.[4] Similar competitive benzoate scissions are now recorded for two other enol carboxylates, isopropenyl $BzO\cdot CMe{:}CH_2$ and α-phenylvinyl benzoate $BzO\cdot CPh{:}CH_2$: in addition, a new minor route has been detected in the pyrolysis of vinyl benzoate.

Vinyl Benzoate.—It was previously concluded [4] that neither type of acyl–oxygen scission (B^1 or B^2) occurs in the pyrolytic breakdown of ester (I). The B^1 variation is here

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[1] Part XIX, Reininger, Ritchie, and Ferguson, preceding paper.

[2] Young, Frostick, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635.

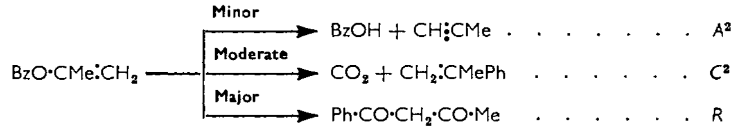
[3] Allan, McGee, and Ritchie, *J.*, 1957, 4700.

[4] Allan, Forman, and Ritchie, *J.*, 1955, 2717.

precluded by the absence of an α-hydrogen atom in the acyl group (though it occurs where this group is aliphatic[3,4]); but, although the B^2 variation is formally possible, neither of its products (benzaldehyde and keten) could be detected. At the time, gas–liquid chromatography was not an available tool: a critical re-examination of the pyrolysis has now shown that a trace of benzaldehyde is formed. Keten itself was not detected, but all its known breakdown products[5] were present. Similarly, chlorobenzaldehydes have been observed by Reininger and Ritchie[6] in slightly greater amount in the pyrolysis of the three vinyl chlorobenzoates; and, although keten again remained undetected, they concluded that very minor B^2 scission occurred.

The major formation of acetophenone from vinyl benzoate was attributed[4] to a primary thermal rearrangement to benzoylacetaldehyde, followed by decarbonylation, but hitherto there has been no direct evidence that any of this labile precursor survives in the pyrolysate. It has now been found that the pyrolysate shows the colour reaction with alcoholic ferric chloride characteristic of the enolic group ·C(OH):CH· which occurs in benzoylacetaldehyde. In addition, a trace of toluene has been detected in the pyrolysate, which may be attributed to partial decarbonylation[7] of the acetophenone.

Isopropenyl Benzoate.—Here the B^2 scission is structurally precluded: the observed products are best interpreted by three primary competitive scissions, only the last of which was recorded by Young *et al.*[2] Several additional products detected in the total



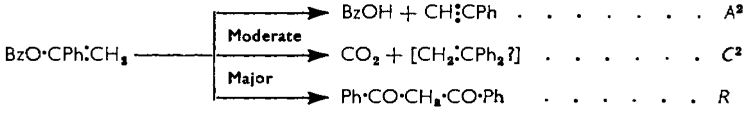
$$\mathrm{BzO{\cdot}CMe{:}CH_2} \begin{cases} \xrightarrow{\text{Minor}} \mathrm{BzOH + CH{:}CMe} & A^2 \\ \xrightarrow{\text{Moderate}} \mathrm{CO_2 + CH_2{:}CMePh} & C^2 \\ \xrightarrow{\text{Major}} \mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}Me} & R \end{cases}$$

pyrolysate agree with minor predictable secondary breakdowns—benzene, from decarboxylation of benzoic acid; propiophenone and ethylbenzene, from successive decarbonylations of the β-diketone, benzoylacetone; ethylene, probably from complex secondary reactions of some of the higher hydrocarbons; and acetone, probably from the following minor secondary reaction (cf. the disproportionation of ethylidene dibenzoate[8]), although the benzoic anhydride which should accompany it could not be detected:

$$\mathrm{BzO{\cdot}CMe{:}CH_2 + BzOH \longrightarrow BzO{\cdot}CMe_2{\cdot}OBz \longrightarrow Bz_2O + COMe_2}$$

There was no evidence that α-methylstyrene from the C^2 scission is accompanied by either of its isomers, β-methylstyrene or allylbenzene, except for small and rather doubtful traces.

α-Phenylvinyl Benzoate.—This ester is more thermostable at *ca.* 500° than the other two. Here, again, B^2 scission is structurally precluded, and the observed products are best interpreted by a scheme of three primary competitive scissions, of which only the last has been recorded by Young *et al.*[2] Additional components detected in the total



$$\mathrm{BzO{\cdot}CPh{:}CH_2} \begin{cases} \xrightarrow{\text{Minor}} \mathrm{BzOH + CH{:}CPh} & A^2 \\ \xrightarrow{\text{Moderate}} \mathrm{CO_2 + [CH_2{:}CPh_2?]} & C^2 \\ \xrightarrow{\text{Major}} \mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}Ph} & R \end{cases}$$

pyrolysate are again due to minor secondary breakdowns—benzene, from decarboxylation of benzoic acid; benzyl phenyl ketone, from a single decarbonylation of dibenzoylmethane (with no detectable amount of the product of a double decarbonylation, diphenylmethane);

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[5] Young, *J.*, 1958, 2909.
[6] Part XVIII, Reininger and Ritchie, *J.*, 1963, 2678.
[7] Smith and Hinshelwood, *Proc. Roy. Soc.*, 1940, *A*, **176**, 468.
[8] Allan, Jones, and Ritchie, *J.*, 1957, 524.

and a trace of acetophenone, probably due to the predictable [8] addition–disproportionation sequence:

$$\mathrm{BzO{\cdot}CPh{:}CH_2 + BzOH \longrightarrow BzO{\cdot}CPhMe{\cdot}OBz \longrightarrow Bz_2O + Ph{\cdot}CO{\cdot}Me}$$

There is an element of doubt about the C^2 reaction. The gaseous pyrolysate contains 26% of carbon dioxide, which is much more than in the pyrolysates from the other two esters and far greater than can be accounted for by decarboxylation of benzoic acid from the minor A^2 scission. It clearly suggests C^2 scission of α-phenylvinyl benzoate as an important competing reaction in the overall breakdown; yet, despite careful search, there was no sign of the predictable accompanying olefin, 1,1-diphenylethylene. This hydrocarbon may have undergone an unexpected secondary breakdown; certainly, the pyrolysate contained an unusually high proportion of uncharacterised carbonised material.

Preparation of Pure Enol Carboxylates.—Earlier work [3] has shown that vinyl benzoate is difficult to prepare in a state of rigorous purity. Indeed, a survey of the literature shows that previous records of this ester quote no really satisfactory elementary analysis and suggests that it may never previously have been prepared in a satisfactorily pure state. High-temperature vapour-phase preparations, such as pyrolysis of ethylene dibenzoate [3,9] and catalysed addition of acetylene to benzoic acid,[10] give a product contaminated with acetophenone (from the R/C^1 breakdown sequence) which is difficult to purify. Three recorded alternative methods, requiring only low or moderate temperatures, have therefore been critically re-examined.

(i) Direct benzoylation of (enolic) acetaldehyde with benzoyl chloride (60°: 1—2 hr.) in presence of a base such as pyridine or dimethylaniline has been claimed by Sladkov and Petrov [11] to give a high yield of vinyl benzoate, six other vinyl esters being similarly prepared; but this method failed completely in our hands.

(ii) Adelman [12] prepared vinyl benzoate by ester interchange between vinyl acetate and benzoic acid, in presence of mercuric sulphate. He recorded that high yield and purity are favoured by low reaction-temperatures, and that the principal contaminant at higher temperatures is ethylidene diacetate, $\mathrm{CHMe(OAc)_2}$, formed by partial interaction of unchanged vinyl acetate with liberated acetic acid. The present work confirms that good yields of extremely pure ester are formed at 35°, with a reaction time of 77 hr.; but, rather unexpectedly, it was found that when the reaction temperature exceeds *ca.* 50° ethylidene diacetate is accompanied by a small amount of ethylene diacetate $\mathrm{(CH_2{\cdot}OAc)_2}$. Mutual addition of vinyl acetate and acetic acid must therefore occur in both possible senses (cf. Tables 1 and 2). A similar effect has recently been noted [13] in ester interchange between vinyl acetate and a commercial mixture of aliphatic C_8—C_{10} acids.

(iii) Nesmeyanov *et al.*[14] observed that enol benzoates may be prepared by the action of benzoyl chloride on halogenomercuri-aldehydes and -ketones. This method has been found suitable for the preparation of vinyl and isopropenyl benzoate in rather low yield but of high purity, gas–liquid chromatography showing only a single sharp peak for each, just as for the low-temperature Adelman method described above.

EXPERIMENTAL

Pyrolysis: Apparatus and Procedure.—The flow-reactor, receivers, and general mode of operation have been described previously.[3,4,8] After each run, the reactor was cleaned by acetone–benzene, and a stream of air was passed through it at *ca.* 450°.

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[9] Chitwood, U.S.P. 2,251,983/1941.

[10] Imperial Chemical Industries Limited, B.P. 581,501/1946.

[11] Sladkov and Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 459.

[12] Adelman, *J. Org. Chem.*, 1949, **14**, 1057.

[13] Jones, " Gas Chromatography 1960," Ed. Scott, Butterworths Scientific Publns., London, 1960, p. 401.

[14] Nesmeyanov and Lutsenko, *Doklady Akad. Nauk S.S.S.R.*, 1948, **59**, 707; Nesmeyanov, Lutsenko, and Tumanova, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1949, 601.

Analytical Methods.—Non-gaseous pyrolysates were normally examined after fractional distillation. Unless otherwise specified, pyrolysate components were identified by gas–liquid chromatography, as described previously.[6]

Preparations.—Vinyl benzoate: Adelman method.[12] Benzoic acid (120 g.) was dissolved in redistilled vinyl acetate (330 g.); mercuric acetate (3·8 g.) and concentrated sulphuric acid (1 ml.) were added, to form the mercuric sulphate catalyst *in situ*, and the whole was heated at 35° for 77 hr. After cooling, the mixture was treated with sodium acetate to neutralise unused acid: fractional distillation yielded the pure ester (99 g., 67%), b. p. 71—73°/3 mm., n_D^{20} 1·5263 (Found: C, 73·2; H, 5·6. Calc. for $C_9H_8O_2$: C, 73·0; H, 5·4%). Table 1 shows the way in which yield and purity of ester decrease as reaction-temperature is raised. Table 2 shows the way in which ethylidene diacetate and ethylene diacetate appear in the product at higher temperatures: the figures refer to the early stages of a run at 75°, aliquot portions of the mixture being removed at intervals and analysed by gas–liquid chromatography, with pure reference samples.

TABLE 1.

Effect of temperature and time of reaction in the preparation of vinyl benzoate by Adelman's method.

			Contaminants	
Temp.	Time (hr.)	Yield (%)	$CHMe(OAc)_2$	$(CH_2{\cdot}OAc)_2$
35°	77	67	Nil	Nil
55	42	51	Moderate	Trace
75	5	23	Major	Minor

TABLE 2.

Effect of reaction time in early stages on yield of esters at 75°.

Time (hr.)	1¼	2½	3¾	5
CH_2:CH·OBz (%)	4·6	10·5	18·4	23·0
$CHMe(OAc)_2$ (%)	—	2·7	5·1	6·4
$(CH_2{\cdot}OAc)_2$ (%)	—	—	2·0	2·2

Vinyl benzoate: Nesmeyanov method.[14] Vinyl acetate (86 g.) was added to mercuric acetate (320 g.) in water (1·5 l.); the precipitate of mercury salts was filtered off, and potassium chloride (75 g.) added to the filtrate. Crystalline chloromercuri-acetaldehyde (196 g., 71%), m. p. 132—133° (lit.,[14] 100%: m. p. 129—130°), was precipitated; this was powdered and suspended in sodium-dried xylene (200 ml.), and benzoyl chloride (100 g.) was slowly added, the mixture being heated at 50° for 6 hr. After cooling, mercuric chloride was filtered off; the crude ester, distilled, was freed from persistent traces of benzoyl chloride by successive treatments with pyridine, dilute acid, aqueous sodium hydrogen carbonate, and water. The product, dried and redistilled, gave pure ester (23 g., 15%), b. p, 78—80°/5 mm., n_D^{20} 1·5283 (Found: C, 73·3; H, 5·5%).

Isopropenyl benzoate: Nesmeyanov method.[14] Chloromercuriacetone (166 g., 57%), m. p. 102—103°, was prepared from isopropenyl acetate (100 g.) as described above (lit.,[14] 75%; m. p. 103—104°), and converted as before into the pure enol benzoate (71 g., 44%), b. p. 62°/2 mm., n_D^{20} 1·516, d_4^{20} 1·045 (lit.,[14] 63%, b. p. 87°/7 mm., n_D^{20} 1·517, d_4^{20} 1·047) (Found: C, 74·1; H, 6·3. Calc. for $C_{10}H_{10}O_2$: C, 74·1; H, 6·2%). Attempts to use the methods of Young *et al.*[2] and Sladkov and Petrov [11] were unsuccessful (the latter probably because of the very low enol content of acetone [15]).

α-Phenylvinyl benzoate: Lees method.[16] Acetophenone (120 g.) and benzoyl chloride (140 g.) were mixed and refluxed for 10 hr. The pure ester (92 g., 41%) had b. p. 140—144°/4 mm., n_D^{20} 1·589 (lit.,[3, 16] b. p. 186—189°/9 mm.) (Found: C, 80·7; H, 5·6. Calc. for $C_{15}H_{12}O_2$: C, 80·5; H, 5·4%). In one preparation by their method, Young *et al.*[3] claim to have obtained the ester as a solid, m. p. 37—38° (not analysed): more probably this was benzoic anhydride, which was obtained (m. p. 38—40°) as a by-product in the preparation described above.

α-Methylpropenyl benzoate: Lees method.[16] Ethyl methyl ketone (2 moles) and benzoyl chloride (1 mole) were mixed and refluxed for 24 hr. The pure *ester* (34%) had b. p. 126°/16

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[15] Schwarzenbach and Wittwer, *Helv. Chim. Acta*, 1947, **30**, 669.

[16] Lees, *J.*, 1903, **83**, 145.

mm., n_D^{20} 1·5170 (Found: C, 74·8; H, 6·5. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). The structure of the ester was not conclusively proved: but the structure $BzO{\cdot}CMe{:}CHMe$ is preferred to that of its isomer $BzO{\cdot}CEt{:}CH_2$ because of the known mode of enolisation of ethyl methyl ketone (cf. also the enol benzoates of methyl n-pentyl ketone and benzyl methyl ketone [2]).

Reference Standards for Chromatography.—Various pure reference standards were required: one of these presents points of interest.

β-*Methylstyrene* (*propenylbenzene*). Allylbenzene was passed through a vapour-phase flow reactor, packed with Pyrex helices coated with ferric oxide, at 250°, and partially isomerised to propenylbenzene, as described by Levina.[17] The isomers in the standard (allylbenzene, b. p. 154—155°: propenylbenzene,[18] b. p. 176—177°) were not separated: but the extent of the isomerisation was estimated chromatographically as *ca.* 45%.

TABLE 3.

Pyrolysis of esters: general results.

Pyrolysand	$CH_2{:}CH{\cdot}OBz$	$CH_2{:}CMe{\cdot}OBz$	$CH_2{:}CPh{\cdot}OBz$
Temp.	500°	500°	510°
Feed-rate (g./min.)	0·30	0·50	0·20
Residence time (sec.)	28	18	63
Wt. pyrolysed (g.)	21·5	14·7	24·0
(*a*) In cold trap (ml.)	*ca.* 0·5	1·0	3·0
(*b*) In main receiver (g.)	16·8	11·8	17·0
(*c*) Gaseous pyrolysate (l.)	1·1	0·8	1·4
Composition (%) of (*c*) (approx.):			
CO	82	84	69
CO_2	9	8	26
Alkenes	2	7	5
Alkynes	7	1	Nil
CH_4	Trace *	Trace *	Trace *

* Identified by infrared spectrometry.

Pyrolysis of the Esters.—Table 3 summarises the general experimental conditions and results; identification of pyrolysate components was by gas–liquid chromatography, retention times being accurately matched against those of synthetic reference standards.

Pyrolysis of Vinyl Benzoate.—Liquid (*a*) was benzene (infrared spectrum). Liquid (*b*), distilled, yielded (i) *ca.* 1 g., b. p. 45—94°, (ii) 3·2 g., b. p. 95—100°, (iii) 6·5 g., b. p. 72—110°/10 mm., (iv) 5 g., b. p. 77—152°/4 mm., and (v) a small residue. Fraction (i) contained benzene; fraction (ii) contained benzene, toluene, and styrene; fraction (iii) contained styrene, acetophenone (2,4-dinitrophenylhydrazone, mixed m. p.), and a trace of benzaldehyde. Fraction (iv) was unchanged benzoate, with some dissolved benzoic acid. Separate portions of liquid (*b*) gave positive tests for acid anhydride (Davidson–Newman reagent [19]) and for an enolic $C(OH){:}CH$ group (alcoholic ferric chloride). Gas (*c*), passed through a 2,4-dinitrophenylhydrazine trap before analysis (Hempel), gave a yellow precipitate, probably due to acetaldehyde; an aniline–ether trap gave no evidence for keten.

Pyrolysis of Isopropenyl Benzoate.—Liquid (*b*), filtered from suspended carbonised matter and set aside, deposited benzoylacetone (4 g., m. p. 58—60°) (infrared spectrum; mixed m. p.). The filtrate, distilled, yielded (i) 2 g., b. p. 33—39°/40 mm., (ii) 1·5 g., b. p. 80—155°/28 mm., (iii) 2 g., b. p. 84—125°/3 mm., and (iv) a small residue. Fraction (i) contained acetone, benzene, α-methylstyrene, possible small traces of an isomer of the latter, and a probable trace of ethylbenzene; fraction (ii) contained propiophenone and unchanged (*b*); fraction (iii) was unchanged benzoate with a little dissolved benzoic acid. (Unchanged pyrolysand yielded acetone and benzoic acid on hydrolysis.) Liquid (*b*) and fraction (iii) gave a negative result to the Davidson–Newman test for acid anhydride. The alkyne in gas (*c*) was propyne (infrared spectrum).

Pyrolysis of α-Phenylvinyl Benzoate.—Product (*b*) was a dark slurry; filtration yielded a solid which on crystallisation from benzene gave dibenzoylmethane as a yellow solid (3·5 g.; m. p. 75—77°) (infrared spectrum; mixed m. p.). The filtrate, distilled, yielded (i) a few drops,

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[17] Levina, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 2287.

[18] Lévy and Dvoleitzka-Gombinska, *Bull. Soc. chim. France*, 1931, **49**, 1765.

[19] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.

b. p. 40—95°, (ii) 7 g., b. p. 85—130°/3 mm., (iii) 2·5 g., b. p. 130—175°/3 mm., (iv) 4 g., b. p. 130—180°/1 mm., and (v) a small residue. Fraction (i) contained benzene and traces of two unidentified components; fraction (ii) contained acetophenone, phenylacetylene, and unchanged ester; fraction (iii) contained unchanged ester, with some dissolved benzoic acid, and fraction (iv) contained benzyl phenyl ketone (2,4-dinitrophenylhydrazone, mixed m. p.) and traces of an unidentified component. The volatile liquid (*a*) was not identified: it boiled a little above room temperature, and its infrared spectrum showed bands at 3800w, 3600w, 2400s, 2200m, 2100m, 1320m, 950w, 740m, 720m, and 675s cm.$^{-1}$.

Infrared Spectra.—The infrared absorption spectra of the following compounds have been recorded: vinyl (D.M.S. Index No. 9913), isopropenyl (D.M.S. Index No. 9914), and α-phenylvinyl benzoate (D.M.S. Index No. 9915), and the benzoate of enolic ethyl methyl ketone (D.M.S. Index No. 9916).

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Chemical Technology Department,
Royal College of Science and Technology, Glasgow. [*Received, September* 11*th*, 1962.]