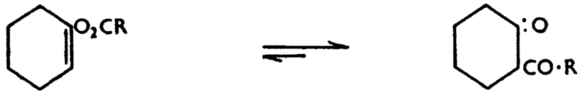
949. *Studies in Pyrolysis. Part XII.*‡ *Reversible Thermal Rearrangement as a Competitive Route in the Pyrolysis of Enol Carboxylates.*

By R. J. P. Allan, J. McGee, and P. D. Ritchie.

The previously described formation of β-diketones by thermal rearrangement[1] of enol carboxylates (other than vinyl esters) is shown to be reversible. In the vapour phase at *ca.* 500° the equilibrium strongly favours the β-diketone. The enol carboxylates studied (*iso*propenyl acetate, *cyclo*hex-1-enyl acetate, and *cyclo*hex-1-enyl benzoate) undergo, in addition to the above change, a series of minor competitive scissions, including decarboxylation to an alkene. By-products are discussed.

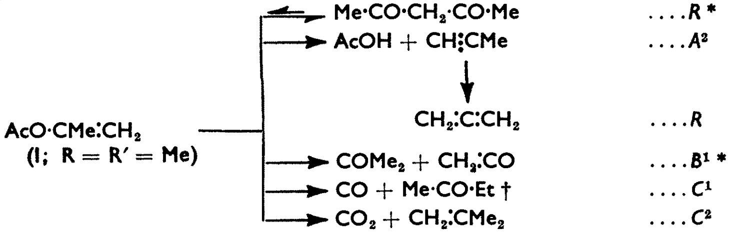
Various enol carboxylates (*e.g.*, I; R = Me, R′ = Me or Ph: II; R = Me) isomerise thermally[1] in the vapour phase at *ca.* 500°, giving good yields of the corresponding β-diketones (III) and (IV) respectively. This is believed[1] to involve a four-centre transition-state, a concept possibly also applicable to a number of other related thermal rearrangements.[2] Work on three enol carboxylates (I; R = R′ = Me), (II; R = Me or Ph) and two of the corresponding β-diketones (III; R = R′ = Me: IV; R = Ph) has now revealed the unexpected fact that the rearrangement *R* is reversible, with the equilibrium point lying far over to the β-diketone side, thus:

(I) $\text{R·CO}_2\text{·CR}'\text{: CH}_2 \rightleftharpoons \text{R·CO·CH}_2\text{·CO·R}'$ (III) . . . *R*

(II)  (IV) . . . *R*

This is clearly demonstrated by pyrolysis of the pure β-diketones (III) and (IV); in each case, the pyrolysate contains *inter alia* a small amount of the corresponding enol carboxylate.

Young *et al.*[1] recorded no by-products from these pyrolyses. It was, however, shown later by Allan, Forman, and Ritchie[3] that vinyl carboxylates [*i.e.*, those enol carboxylates (I) in which R′ = H] break down under similar conditions by a complex series of competitive scissions; we have demonstrated that this is true of enol carboxylates in general. The best overall interpretation of the results is offered by the following schemes, in which * indicates a major route and † a product identified in the pyrolysate from the ester only, not from the β-diketone:



(*Also small amounts of* Ac_2O, CH_4, *and* $CH_2{:}CH_2$)

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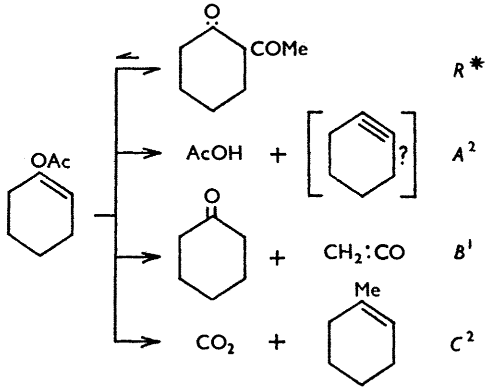
‡ Part XI, *J.*, 1957, 2564.

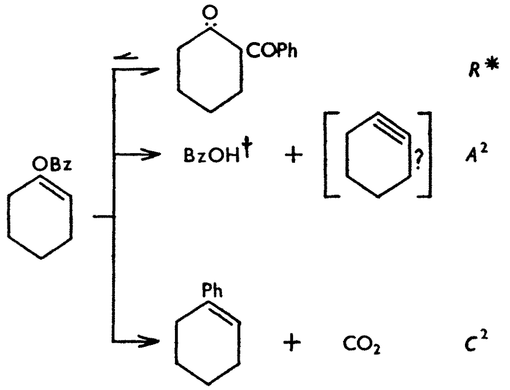
[1] Young, Frostick, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635; Boese and Young, U.S.P. 2,395,800/1946, B.P. 615,523/1949.

[2] See, *e.g.*, Chapman, *J.*, 1927, 1743; Schönberg *et al.*, *Ber.*, 1930, **63**, 178; *Annalen*, 1930, **483**, 107; Wiberg *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 2665; 1955, **77**, 2205, 2774; White, *ibid.*, 1955, **77**, 6011, 6014; Al-Kazami, Tarbell, and Plant, *ibid.*, 1955, **77**, 2479.

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



(Also CO, *and small amounts of* Ac_2O, $COMe_2$, $CH_2{:}CH_2$, *and cyclohexene)*



(Also CO, $CH_2{:}CH_2$, *benzene, and cyclohexanone*

DISCUSSION

Rearrangement (*R*).—In all cases studied, the β-diketone is the major product from pyrolysis of the ester. Further, in agreement with this, the pure diketone is found to be more thermostable than its parent ester: its pyrolysis under the same conditions gives only a minor overall breakdown, though the formation of a small amount of enol carboxylate is proved by a combination of chemical and spectrometric methods.

Allan *et al.*[3] showed that the competitive scissions undergone by vinyl esters include a decarbonylation occurring in two stages, (i) a primary rearrangement (*R*), similar to that described above, but yielding a labile β-keto-aldehyde instead of a stable β-diketone, followed by (ii) a decarbonylation (C^1) of the rearrangement product. (This C^1 reaction is predictable for aldehydes, but not in general for ketones.) Here, also, *R* may possibly by an equilibrium process, the two-stage sequence being formulated thus:

$$R{\cdot}CO_2{\cdot}CH{:}CH_2 \underset{?}{\overset{R}{\rightleftharpoons}} [R{\cdot}CO{\cdot}CH_2{\cdot}CHO] \xrightarrow{C^1} CO + R{\cdot}CO{\cdot}Me$$

However, the instability of the intermediate will here displace the equilibrium still further away from the ester, virtually precluding detection of the latter in a separate pyrolysis of the pure β-keto-aldehyde. It has, in fact, already been shown [3] that benzoylacetaldehyde (III; R = Ph, R′ = H) is almost completely decarbonylated at *ca.* 550°, and, although a little survives at *ca.* 400°, re-examination of the infrared spectrum of the pyrolysate has shown no trace of the corresponding enol carboxylate, vinyl benzoate.

Bailey *et al.*[4] have shown that carbonised deposits (presumed to be acidic) formed during pyrolysis of an ester can catalytically induce rearrangement of certain of the primary products, notably olefins. No carbonisation was reported by Young *et al.*,[1] but in the present work it was found that carbonisation, though slight, was unavoidable at the high temperatures necessary for scission, so that carbonised deposits may possibly affect catalytically the competitive scissions noted. Certainly, the rearrangement (*R*) of enol carboxylates can be caused not only thermally, but also catalytically (*e.g.*, by bases [5] or boron trifluoride,[1] though in the special case of vinyl esters the latter causes violent polymerisation, even at −40°, rather than detectable rearrangement [6]).

A^2*Scission.*—It is not certain whether methylacetylene and allene are both formed directly (*i.e.*, competitively) from *iso*propenyl acetate, or whether one is the precursor of the other. Hurd *et al.*[7] showed that an alk-1-yne is partially isomerised to an alka-1 : 2-diene at *ca.* 500°, but that the reverse change does not appear to occur thermally (though it can be

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[4] Bailey *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 73, 75, 357.

[5] Claisen and Haase, *Ber.*, 1903, **36**, 3674; Dieckmann and Stein, *Ber.*, 1904, **37**, 3370.

[6] Allan, Ph.D. Thesis, Glasgow University, 1956, p. 51.

[7] Meinert and Hurd, *J. Amer. Chem. Soc.*, 1930, **52**, 4549; Hurd and Meinert, *ibid.*, 1931, **53**, 292; Hurd and Christ, *ibid.*, 1937, **59**, 2161.

induced catalytically). This, coupled with the fact that an alkyne is formed from vinyl[3] as well as from *iso*propenyl acetate, by a minor scission, suggests that methylacetylene is a primary product of the latter, with subsequent partial isomerisation (*R*) to allene, as indicated in the above scheme. Nevertheless, another possibility cannot be excluded. Formally, the acetoxy-group of *iso*propenyl acetate may, on elimination, abstract a β-hydrogen atom from either of two dissimilar sites; the work of Bailey *et al.*[4] suggests that one of these (the α-methyl group) should be favoured when the reaction vessel is clean, yielding allene directly in the early stages of the pyrolysis, by what is essentially an A^1 rather than an A^2 scission, whereas the other site (the methylene group) should become increasingly favoured as carbonisation develops, yielding methylacetylene by direct A^2 scission in the later stages.

By analogy with these results, it seems that the acid formed on pyrolysis of the *cyclo*hex-1-enyl carboxylates should be accompanied by an acetylene (*cyclo*hexyne) and an allene (*cyclo*hexa-1 : 2-diene). As expected, there was no evidence for these transient entities (*cyclo*hexyne is [8] incapable of stable existence); but neither was there evidence for any of their probable secondary reactions—for example, rearrangement to *cyclo*hexa-1 : 3-diene, trimerisation to dodecahydrotriphenylene, or disproportionation to benzene plus *cyclo*hexene. (Benzene is obtained from the benzoate *only*, and *cyclo*hexene from the acetate *only*.) This A^2 reaction is therefore less well established than that of *iso*propenyl acetate, though it is difficult to account for the observed carboxylic acid on any other basis.

B^1 Scission.—This reaction, though structurally precluded for an enol benzoate, competes quite strongly in the pyrolysis of the two acetates (cf. the corresponding results[3] for vinyl benzoate and acetate). Both the acetates also yield a trace of acetic anhydride, probably formed by interaction of acetic acid (route A^2) and keten (route B^1). At least one ester, benzyl benzoate, yields[9] an acid anhydride and an ether, by disproportionation (*D*); but the *D* reaction is an unlikely origin for the anhydride now observed, since *cyclo*hex-1-enyl benzoate yields no benzoic anhydride, and vinyl carboxylates[10] no divinyl ether.

C^1 Scission.—Formation of a trace of ethyl methyl ketone from *iso*propenyl acetate is unexpected. No simple rearrangement of the type discussed could lead to a readily decarbonylated β-keto-aldehydic precursor such as $Me{\cdot}CO{\cdot}CHMe{\cdot}CHO$ or $Et{\cdot}CO{\cdot}CH_2{\cdot}CHO$ (the latter is claimed[3] as the direct precursor of the ethyl methyl ketone formed on pyrolysis of ethylene dipropionate[11]). Conceivably, the ketone might arise by direct semidecarbonylation of acetylacetone, but this is unlikely since it was not detected when the equilibrium system was approached from the β-diketone side by pyrolysis of pure acetylacetone, a negative result which agrees with an earlier study of this pyrolysis.[12] The explanation may lie in the following tentative sequence of high-temperature free-radical reactions, in which the *iso*propenyloxy-radical (${\cdot}O{\cdot}CMe{:}CH_2$), formed by the initial scission, reacts preferentially (at least in part) in its alternative canonical form, the acetonyl radical ($O{:}CMe{\cdot}CH_2{\cdot}$), thus:

$$\text{(i)}\quad Me{\cdot}CO{\cdot}O{\cdot}CMe{:}CH_2 \longrightarrow Me{\cdot}CO{\cdot} + {\cdot}O{\cdot}CMe{:}CH_2$$

$$\text{(ii)}\quad Me{\cdot}CO{\cdot} \longrightarrow Me{\cdot} + CO$$

$$\text{(iii)}\quad {\cdot}O{\cdot}CMe{:}CH_2 \longleftrightarrow O{:}CMe{\cdot}CH_2{\cdot}$$

$$\text{(iv)}\quad O{:}CMe{\cdot}CH_2{\cdot} + Me{\cdot} \longrightarrow Me{\cdot}CO{\cdot}CH_2{\cdot}Me$$

However, although this type of free-radical sequence seems equally applicable to *cyclo*hex-1-enyl acetate, pyrolysis of the latter (Table 2, runs 10—12) yields no evidence

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[8] Rodd, " Chemistry of Carbon Compounds," Elsevier, London, 1954, Vol IIa, p. 5; Favorsky and Boshowsky, *Annalen*, 1912, **390**, 122; Favorsky, *Bull. Soc. chim. France*, 1936, (v), **3**, 1727.

[9] Hurd and Bennett, *J. Amer. Chem. Soc.*, 1929, **51**, 1197.

[10] See ref. 3, p. 2721.

[11] Chitwood, U.S.P. 2,251,983/1949.

[12] Hurd and Tallyn, *J. Amer. Chem. Soc.*, 1925, **47**, 1779.

for formation of 2-methyl*cyclo*hexanone, which on the above basis should be the ketonic product of a C^1 scission.

C^2 Scission.—The present work adds three examples to the growing list[13] of C^2 scissions, believed until recently to occur only rarely in ester pyrolysis.

Unexplained Products.—The trace of acetone formed from *cyclo*hex-1-enyl acetate, and the larger amount of *cyclo*hexanone from the corresponding benzoate, are presumably due to a complex free-radical mechanism. Since the benzoate was rigorously dried before pyrolysis, a partial hydrolysis by adventitious water cannot be responsible for the concurrent formation of ketone and a trace of benzoic acid. The benzene which is a by-product from the pyrolysis of *cyclo*hex-1-enyl benzoate clearly arises from the aroyl half of the ester molecule, rather than from the *cyclo*alkenyl half by some type of dehydrogenation, since it is not formed from the corresponding acetate, whereas the reverse holds for

TABLE 1. *Pyrolysis of* iso*propenyl acetate* (I; R = R′ = Me) *and acetylacetone* (III; R = R′ = Me).

Pyrolysand	(I; R = R′ = Me)			(III; R = R′ = Me)					
Run No.	1	2	3	4	5	6	7 †	8	9
Temp.	500°	500°	500°	550°	500°	500°	500°	450°	400°
Feed-rate (g./min.)	0·33	0·20	0·19	0·15	0·40	0·20	0·20	0·20	0·14
Contact time (sec.)	14	24	25	30	12	24	24	25	39
Wt. pyrolysed (g.)	60·0	30·0	57·0	50·0	50·0	73·4	50·0	10·0	10·0
(*a*) In cold trap (ml.)	6·0	3·0	6·0	1·5	Nil	Nil	0·5	Nil	Nil
(*b*) In main receiver (g.)	53·6	27·0	53·2	40·0	46·5	62·5	39·1	9·2	9·0
(*c*) Gaseous pyrolysate (l.)	1·8	1·3	2·7	5·3	1·0	4·3	3·8	0·3	0·1
Composition (%) of (*c*) (approx.):									
CO	87	63	80	63	60	59	57	—	—
CO_2	10	20	16	22	20	29	29	—	—
Unsat. hydrocarbons	3	17	4	15	20	12	14	—	—
CH_4	—	—	—	*	—	*	*	—	—
CO : CO_2 (molar ratio)	8·7	3·2	5·0	2·9	3·0	2·0	2·0	—	—

* Traces observed by infrared spectrometry. † Carbonised reaction vessel from Run 6 used.
— Not observed.

TABLE 2. *Pyrolysis of* cyclo*hex-1-enyl acetate* (II; R = Me), cyclo*hex-1-enyl benzoate* (II; R = Ph), *2-benzoyl*cyclo*hexanone* (IV; R = Ph), *and* cyclo*hexanone; copyrolysis of* cyclo*hexanone and benzoic acid.*

Pyrolysand	(II; R = Me)			(II; R = Ph)			(IV; R = Ph)			*cyclo*Hexanone	
										Alone	With benzoic acid ‡
Run No.	10	11	12	13	14	15	16	17	18	19	20
Temp.	500°	500°	500°	480°	500°	500°	500°	500°	500°	500°	500°
Feed-rate (g./min.)	0·27	0·23	0·51	0·30	0·29	0·22	0·25	0·32	0·25	0·20	0·45
Contact time (sec.)	25	29	13	17	20	44	23	30	38	23	11
Wt. pyrolysed (g.)	30·0	27·0	61·0	40·0	40·0	30·0	14·0	30·0	30·0	32·0	42·6
(*a*) In cold trap (g.)	†	†	†	†	†	2·0	†	Nil	Nil	†	Nil
(*b*) In main receiver (g.)	25·2	24·0	58·0	36·0	39·0	27·0	11·0	21·5	21·4	31·5	41·6
(*c*) Gaseous pyrolysate (l.)	1·7	2·1	2·3	1·5	2·0	4·2	0·5	2·9	4·6	0·25	0·4
Composition (%) of (*c*) (approx.):											
CO	69	63	—	78	85	69	63	71	—	57	60
CO_2	9	9	—	11	9	12	20	16	—	5	9
Unsat. hydrocarbons	22	28	—	11	6	19	17	13	—	38	31
CH_4	—	*	—	—	—	*	—	—	*	—	—
CO : CO_2 (molar ratio)	7·7	7·0	—	7·1	9·4	5·7	3·2	4·4	—	11·4	6·5

* Traces observed by infrared spectrometry. † No cold trap used.
‡ Sat. solution (ketone 25·9 g., acid 16·7 g.). — Not observed.

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[13] For summary, see Mackinnon and Ritchie, *J.*, 1957, 2564.

the formation of *cyclo*hexene. Decarboxylation of benzoic acid formed by the A^2 scission may, of course, contribute to the formation of benzene; but this can be only a minor reaction, since copyrolysis of a mixture of benzoic acid and *cyclo*hexanone, under the same conditions, leads to very little decomposition of either component (Table 2, run 20).

Another product of doubtful origin is ethylene. It has been obtained from vinyl esters [3] and ethers,[14] where free-radical reactions at a vinyl group may be responsible, but in the three present examples it must have some other origin—possibly (for the two acetates) partial breakdown of keten [15] from the major B^1 scission, or (for the two *cyclo*hex-1-enyl esters) breakdown of a labile intermediate such as the postulated *cyclo*hexyne.

Again, though carbon monoxide is produced in quantity by the *cyclo*hex-1-enyl esters, its origin is not immediately clear. Secondary C^1 scission of the primary β-diketones seems to be excluded (see remarks on C^1 scission), but secondary partial breakdown of the observed *cyclo*hexanone may be responsible, since this ketone yields [16] carbon monoxide on pyrolysis (cf. Table 2, run 19). In addition, partial secondary breakdown of keten [15] may contribute to formation of carbon monoxide from the enol acetates. Whatever the source of the carbon monoxide, it is the major component of the gaseous pyrolysate in each case now studied; the $CO : CO_2$ molar ratio always lies within the range *ca.* 2—9 (cf. Tables 1 and 2).

Since several of the observed products might formally originate both from the enol carboxylate and from its isomeric β-diketone, it is difficult to say whether they arise, in practice, from both sides of the equilibrium system or from one only. For example, formation of keten and (enolic) acetone directly from *iso*propenyl acetate (B^1 scission) is strongly favoured by (i) the larger amounts obtained when equilibrium is approached from the ester side, and (ii) the analogous formation of keten from vinyl acetate and *iso*butyrate,[3] whose rearrangement product is here too unstable to be a significant source of the keten. Ambiguity is introduced, however, by the fact (also observed by Hurd and Tallyn [12]) that small amounts of keten and acetone are formed on pyrolysis of pure acetylacetone, which is quite in accordance with the well-known thermal scission of acetone to keten and methane. There is, on the other hand, much less ambiguity if a trace of a substance is detected on pyrolysing (say) the ester but not the corresponding β-diketone, as, for example, in the formation of benzoic acid from *cyclo*hex-1-enyl benzoate, and of ethyl methyl ketone from *iso*propenyl acetate.

EXPERIMENTAL

Apparatus and Procedure.—The system of reaction vessels, traps, and receivers has already been described.[3] Before each run, the flow system was several times evacuated and flushed with nitrogen to avoid combustion effects during pyrolysis; except where otherwise stated, carbonised deposits were removed after each run by heating the vessel to *ca.* 500° in a current of air.

Analytical Methods: *Results.*—Tables 1 and 2 summarise the general overall conditions and results for 20 runs. Contact times were calculated as previously.[17] The liquid (*a*, *b*) and gaseous (*c*) pyrolysates were analysed by standard chemical methods, supplemented by infrared and ultraviolet spectrometry. In a few cases, where no published infrared spectra could be traced, reference compounds were synthesised and their absorption spectra measured. Keten was characterised as acetanilide (aniline–ether trap), simple aldehydes and ketones as their 2 : 4-dinitrophenylhydrazones (mixed m. p. and/or paper chromatography [18]), acetic acid as acetanilide, and benzene as *m*-dinitrobenzene. Acid anhydrides were detected by the Davidson–Newman colour reaction [19] and by infrared spectrometry. All solids were identified by

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[14] Iengar and Ritchie, *J.*, 1956, 3563.

[15] Peytral, *Bull. Soc. chim. France*, 1921, (iv), **31**, 122.

[16] Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 258; Hurd, Greengard, and Roe, *J. Amer. Chem. Soc.*, 1939, **61**, 3359.

[17] Allan, Jones, and Ritchie, *J.*, 1957, 524.

[18] Burton, *Chem. and Ind.*, 1954, 576.

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

mixed m. p. Gases were analysed by the Hempel method: all results are reported on a nitrogen-free basis. In some runs, a trace of methane was detected by infrared spectrometry, though masked by the excess of nitrogen during Hempel analysis.

Preparation of Pyrolysands.—iso*Propenyl acetate.* Pure ester (L. Light & Co. Ltd.) was redistilled: the fraction used had b. p. 92—94°, n_{D}^{20} 1·406.

Acetylacetone. Pure diketone (L. Light & Co. Ltd.) was redistilled: the fraction used had b. p. 134—139°, n_{D}^{18} 1·452.

cyclo*Hex-*1*-enyl acetate.* The ester, prepared as described by Bedoukian,[20] had b. p. 180—182°, 92°/34 mm., and n_{D}^{20} 1·464 (lit.,[20] b. p. 74—76°/17 mm., n_{D}^{25} 1·4585) (Found: C, 68·6; H, 8·8. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·6%). The ester showed major infrared absorption bands at *ca.* 2941s, 2857m, 1767s, 1695m, 1449m, 1443m, 1366s, 1217s, 1121s, 1073m, 1043m, 1010m, and 905m cm.$^{-1}$.

cyclo*Hex-*1*-enyl benzoate.* Attempts to prepare this compound by ester-interchange between *cyclo*hex-1-enyl acetate and benzoic acid, or by direct Schotten–Baumann benzoylation of (enolic) *cyclo*hexanone, were unsuccessful. Ultimately, it was prepared as described by Nesmeyanov, Lutsenko, and Tumanova.[21] *cyclo*Hex-1-enyl acetate was converted into 2-chloromercuri*cyclo*hexanone (m. p. 134—135°) which was dried and treated with freshly distilled benzoyl chloride in sodium-dried xylene (50°; 12 hr.; rapid stirring). The product was fractionated, washed free from mercuric chloride (dilute ammonia), and refractionated, yielding pure (II; R = Ph), b. p. 138—142°/2 mm., 144—145°/7 mm., n_{D}^{20} 1·547 (lit.,[21] b. p. 146—147°/6 mm., n_{D}^{20} 1·5386) (Found: C, 77·1; H, 7·2. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 6·9%). It appears that the use of rigorously dry xylene is important; this precaution led to yields of *ca.* 40% (Nesmeyanov *et al.*[21] claim 63%), whereas various preparations in which ordinary technical xylene was used gave yields of only *ca.* 5—10%. The ester showed major infrared absorption bands at *ca.* 1730s, 1595m, 1308(shoulder), 1250s, 1215(shoulder), 1120s, 1068m, 1029m, and 710m cm.$^{-1}$.

2*-Benzoyl*cyclo*hexanone.* This was prepared as described by Hauser, Ringler, Swarmer, and Thomson,[22] who claim a yield of 69%. Preliminary work gave very low yields, but the use of 3 instead of 2 equiv. of fresh sodamide, with heating for 12 hr. (water-bath), gave a yield of 22%. The diketone had m. p. 88—89° (needles from ethanol or light petroleum: lit.,[22] m. p. 88—89°) and b. p. 160—166°/1 mm. (Found: C, 77·2; H, 7·3. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 6·9%). It showed major infrared absorption bands at *ca.* 1709s, 1672s, 1600 m, 1580m, 1361s, 1316m, 1282s, 1250s, 1236s, 1183s, 1129s, 1104m, 1072m, 958m, 913m, 787m, 744s, 693m, and 684s cm.$^{-1}$.

Preparation of Reference Compounds for Infrared Spectrometry.—1*-Methyl*cyclo*hexene.* The olefin, prepared as described by Sabatier and Mailhe,[23] had b. p. 110—112°, n_{D}^{15} 1·458 (lit.,[23] b. p. 110·5—111°, n_{D}^{12} 1·458) and showed major infrared absorption bands at *ca.* 1442s, 1370m, 1305m, 1260m, 1135s, 1089s, 1050s, 1014s, 960m, 910s, 890s, 855m, 820s, 790s, and 750s cm.$^{-1}$, in good agreement with published figures.[24]

1*-Phenyl*cyclo*hexene.* Prepared as described by Sabatier and Mailhe,[23] it had b. p. 126—128°/18 mm., n_{D}^{14} 1·569 (lit.,[23] b. p. 129—130°/20 mm., n_{D}^{14} 1·5676) (Found: C, 91·2; H, 9·2. Calc. for $C_{12}H_{14}$: C, 91·1; H, 8·9%) and showed major infrared absorption bands at *ca.* 1600m, 1494s, 1445s, 754s, 734s, and 685m, cm.$^{-1}$.

Pyrolysis of iso*Propenyl Acetate.*—*Runs* 1—3. The analytical results of these runs were similar; those for Run 1 are given as typical. Liquid (*a*) contained acetone. Liquid (*b*), distilled, yielded eight fractions, (i) 6·2 g., b. p. 60—86°, (ii) 7·1 g., b. p. 86—100°, (iii) 13·3 g., b. p. 100—126°, (iv) 20·3 g., b. p. 126—148°, (v) 1 g., b. p. 148—164°, (vi) *ca.* 1 g., b. p. 48—60°/1·3 mm., (vii) *ca.* 0·5 g., b. p. 60—84°/1·3 mm., and (viii) *ca.* 0·2 g., b. p. 84—96°/1·3 mm. There was a small tarry residue. Fractions (i), (ii), and (iii) contained acetone, ethyl methyl ketone, and acetic acid respectively. Fraction (iv) contained acetylacetone (semicarbazone) and an acid anhydride (colour reaction [19]); fraction (v) was similar. Fractions (vi) and (vii) appeared to be mainly acetylacetone contaminated with a little tar. The exit gases (*c*) contained keten (aniline–ether trap), together with methylacetylene, ethylene, and a

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[20] Bedoukian, *J. Amer. Chem. Soc.*, 1945, **67**, 1430.

[21] Nesmeyanov, Lutsenko, and Tumanova, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1949, 601.

[22] Hauser, Ringler, Swarmer, and Thomson, *J. Amer. Chem. Soc.*, 1947, **69**, 2649.

[23] Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 1321.

[24] Amer, Petroleum Inst., Research Project 44, Nat. Bur. Stand., Washington, Serial No. 897, 1949.

trace of methane (infrared). There was no evidence for allene, and *iso*butene could not be detected with certainty. However, the authors are indebted to Dr. R. G. A. New for additional results observed in the Blackley Laboratories of Imperial Chemical Industries Limited, where it was found that liquid (*a*) from the cold trap (several runs, bulked), on fractionation in a Podbielniak column, yielded allene (b. p. −32°), methylacetylene (b. p. −23°), and *iso*butene (b. p. −6°). These fractions were separately brominated, and the bromo-derivatives identified; in addition, the silver salt of methylacetylene was prepared from the second fraction. (Dr. New's results confirm the present work in all other details.)

Pyrolysis of Acetylacetone.—Runs 4—6. The analytical results for Run 4 are given as typical. Liquid (*a*) was mainly acetone. Liquid (*b*), distilled, yielded five fractions, (i) 13·1 g., b. p. 54—72°, (ii) 0·7 g., b. p. 82—100°, (iii) 2·2 g., b. p. 110—130°, (iv) 20·1 g., b. p. 130—150°, and (v) 1·0 g., b. p. 150—160°. There was a small tarry residue. Fraction (i) was mainly acetone; there was no evidence for ethyl methyl ketone in fraction (ii), and evidence for *iso*propenyl acetate (infrared, ultraviolet) was inconclusive (see, however, Run 7); fraction (iii) contained acetic acid; fractions (iv) and (v) were mainly unchanged acetylacetone, containing a little acetic anhydride (colour reaction [19]). The exit gases (*c*) contained keten.

Run 7. Liquid (*a*) contained acetone; the exit gases (*c*) contained keten. Liquid (*b*), dissolved in ether, was washed free from acid with aqueous sodium hydrogen carbonate; the ether layer, dried and freed from ether, yielded four fractions on distillation: (i) *ca.* 0·5 g., b. p. 54—86°, (ii) *ca.* 0·7 g., b. p. 86—100°, (iii) *ca.* 0·8 g., b. p. 100—110°, and (iv) *ca.* 1 g., b. p. 110—112°. There was a small tarry residue. Fractions (i)—(iii) contained unchanged acetylacetone (ultraviolet absorption band, $\lambda_{max.}$ 273), together with *iso*propenyl acetate (ultraviolet absorption band, $\lambda_{max.}$ 206, and infrared bands at *ca.* 1745 and 1200 cm.$^{-1}$). Control experiments showed that these bands characteristic of *iso*propenyl acetate persisted strongly when a sample of pure ester was progressively diluted, down to a concentration of 8%, by addition of acetylacetone. Also, a control sample of pure acetylacetone, treated as above with ether and aqueous sodium hydrogen carbonate, showed none of the absorption bands of the ester, showing that the observed enol carboxylate was not produced by an alkali-catalysed rearrangement of the diketone. The exit gases (*c*), passed through ammoniacal cuprous chloride, gave a red precipitate; the presence of methylacetylene was confirmed by observation of infrared absorption bands at *ca.* 2155m, 1462m, 1452m, 1269w, and 920w cm.$^{-1}$ (lit.,[25] 2160, 1459, 1448, 1264, and 921 cm.$^{-1}$). Ethylene and a trace of methane were also present.

Runs 8 *and* 9. Below 500° pyrolysis was very slight; there was almost no carbonisation in the reaction vessel, and no trace of *iso*propenyl acetate in the pyrolysate (*b*).

Pyrolysis of cyclo*Hex*-1-*enyl Acetate.—Run* 10. The exit gases contained keten, acetone vapour (2 : 4-dinitrophenylhydrazine trap), and ethylene and methane (infrared). Liquid (*b*), distilled, yielded six fractions: (i) 1·0 g., b. p. 74—90°, (ii) 0·8 g., b. p. 90—130°, (iii) 2·0 g., b. p. 130—150°, (iv) 6·5 g., b. p. 150—160°, (v) 8·5 g., b. p. 86—100°/28 mm., and (vi) 6·0 g., b. p. 110—114°/28 mm. There was a small tarry residue (*ca.* 0·5 g.). Fraction (i) contained acetone; there was also evidence for an olefin (ultraviolet). Fraction (ii) contained acetic acid and anhydride (infrared); fraction (iii) contained acetic anhydride (infrared; colour reaction [19]) and *cyclo*hexanone; fraction (iv) contained acetic anhydride (trace), *cyclo*hexanone, and unchanged pyrolysand (infrared). (Separate tests showed that although the *pure* pyrolysand yields *cyclo*hexanone 2 : 4-dinitrophenylhydrazone, owing to its partial hydrolysis by the test reagent even in the cold, this source of possible error is eliminated if the ketone is first separated from the rest of the fraction by aqueous sodium hydrogen sulphite, hydrolysis of the ester under these conditions being negligible.) Fraction (v) was unchanged pyrolysand, and fraction (vi) 2-acetyl*cyclo*hexanone. On treatment with semicarbazide hydrochloride, fraction (vi) yielded a crystalline derivative, m. p. 156—157° [Found: C, 60·1; H, 7·0; O (direct), 8·7; *M* (cryoscopic in benzene), 203, 182]; an authentic sample of 2-acetyl*cyclo*hexanone, prepared as described by Levine *et al.*[26] (b. p. 110°/19 mm., n_D^{20} 1·510; lit.,[27] b. p. 111—112°/18 mm., n_D^{20} 1·5138), yielded the same derivative, m. p. and mixed m. p. 157—159°. Leser [27] has described a so-called semicarbazone of (IV; R = Me), m. p. 159°; in a later paper [28] he gives m. p. 162—163°, but in neither case is an analysis reported. It is now clear that the derivative is

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[25] Amer. Petroleum Inst., Research Project 44, Nat. Bur. Stand., Washington, Serial No. 45, 1943.

[26] Levine, Conroy, Adams, and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1510.

[27] Leser, *Compt. rend.*, 1905, **141**, 1032.

[28] *Idem, Ann. Chim.* (*France*), 1912, **26**, 233.

not, in fact, the expected semicarbazone, but a dehydration product thereof (Calc. for $C_9H_{13}ON_3$: C, 60·3; H, 7·3; O, 8·9; N, 23·5%; *M*, 179. Calc. for $C_9H_{15}O_2N_3$: C, 54·8; H, 7·7; O, 16·2; N, 21·3%; *M*, 197). The compound loses its nitrogen, on analysis, with some difficulty, and reliable figures could not be obtained (Found: N, *ca.* 20% by micro-Dumas, *ca.* 10% by micro-Kjeldahl). There are several formal possibilities for cyclodehydration of the semicarbazone; it is hoped to publish a note on this compound.

Run 11. This gave similar results; in addition, the first fraction (1·5 g., b. p. 40—72°) obtained by distillation of liquid (*b*) contained 1-methyl*cyclo*hexene (its infrared spectrum showed all the 15 absorption bands listed above for the pure olefin) and *cyclo*hexene (infrared).

Run 12. Liquid (*b*), distilled, yielded seven fractions, (i) 0·5 g., b. p. 56°, (ii) 2·0 g., b. p. 78°, (iii) 0·8 g., b. p. 78—130°, (iv) 2·0 g., b. p. 130—150°, (v) 3·8 g., b. p. 150—160°, (vi) 40·2 g., b. p. 62—88°/24 mm., and (vii) 5·7 g., b. p. 106—110°/24 mm. There was a small tarry residue (*ca.* 1·0 g.). Fraction (i) contained acetone. Fraction (ii), treated with tetranitromethane,[29] gave a yellow colour (*cyclo*hexene gives a yellow and *cyclo*hexa-1 : 3-diene a red colour); redistilled, fraction (ii) had b. p. 78—81°, n_D^{20} 1·440, and yielded adipic acid on oxidation (alkaline permanganate), confirming the presence of *cyclo*hexene. Fraction (ii) also contained a trace of acetone and *cyclo*hexanone. Fractions (iii)—(vii) confirmed the results from Run 10.

In Runs 10—12, 2-methyl*cyclo*hexanone was carefully sought by paper chromatography [18] of the mixed 2 : 4-dinitrophenylhydrazones of the overall ketonic products, the 2 : 4-dinitrophenylhydrazone of this ketone being used as control; no evidence for its presence could be obtained.

Pyrolysis of cyclo*Hex-*1*-enyl Benzoate.—Runs* 13 *and* 14. These two exploratory runs gave similar results; those of Run 13 are given here. Liquid (*b*) slowly deposited a few long needles of 2-benzoyl*cyclo*hexanone, m. p. 89—91° (Found: C, 77·4; H, 7·1. Calc. for $C_{13}H_{14}O_2$: C, 77·3; H, 6·9%). Distillation of the filtrate gave three fractions, (i) 5 g., b. p. 42—140°/1 mm., (ii) 18 g., b. p. 140—160°/1 mm., (iii) 5 g., b. p. 160—166°/1 mm., and 4 g. of tar. Fraction (i) contained *cyclo*hexanone; fraction (ii) was mainly unchanged pyrolysand; fraction (iii) was 2-benzoyl*cyclo*hexanone, which solidified on standing, and yielded the pure diketone on recrystallisation, m. p. 89—91° (Found: C, 77·4; H, 7·1%).

Run 15. Liquid (*a*) was mainly benzene, though surprisingly a little *cyclo*hexanone was also found in the cold trap. Liquid (*b*), distilled, yielded seven fractions, (i) 6·2 g., b. p. 78—84°, (ii) 1·7 g., b. p. 84—144°, (iii) 1·4 g., b. p. 144—148°, (iv) 0·9 g., b. p. 20—90°/3 mm., (v) 1·5 g., b. p. 90—120°/3 mm., (vi) 8·7 g., b. p. 120—140°/3 mm., and (vii) 4·0 g., b. p. 140—164°/3 mm. There was *ca.* 1·5 g. of tarry residue. Fraction (i) was mainly benzene, with a little *cyclo*hexanone; fractions (ii) and (iii) were mainly *cyclo*hexanone. Fraction (iv) contained 1-phenyl*cyclo*hexene; its infrared spectrum showed all the 6 absorption bands listed above for the pure olefin. Fraction (v) was mainly unchanged pyrolysand (infrared), from which a trace of benzoic acid separated during the distillation; fractions (vi) and (vii) consisted of a mixture of unchanged pyrolysand (*ca.* 4·5 g.; infrared) and 2-benzoyl*cyclo*hexanone (*ca.* 8·2 g.), the latter separating out on standing.

Pyrolysis of 2*-Benzoyl*cyclo*hexanone.—Runs* 16—18. These three runs gave similar analytical results; those of Run 16 are given as typical. Liquid (*b*) was filtered free from suspended unchanged pyrolysand; the filtrate, distilled, yielded five fractions, (i) 2·3 g., b. p. 78—84°, (ii) 2·5 g., b. p. 84—168°, (iii) 1·6 g., b. p. 76—130°/2 mm., (iv) 4·4 g., b. p. 130—150°/2 mm., and (v) 1·1 g., b. p. 150—162°/2 mm. There was a small tarry residue (*ca.* 2 g.). Fraction (i) was mainly benzene (characterised as *m*-dinitrobenzene), containing no *cyclo*hexa-1 : 3-diene (infrared; no adduct with maleic anhydride); fraction (ii) was mainly *cyclo*hexanone. Fraction (iii) contained *cyclo*hex-1-enyl benzoate (infrared spectrum showed all 10 absorption bands listed above for the pure ester), 1-phenyl*cyclo*hexene (infrared spectrum showed all 6 absorption bands listed above for the pure olefin), but no benzoic acid. Fractions (iv) and (v) solidified on standing, and consisted of unchanged pyrolysand. The exit gases (*c*) contained ethylene (infrared).

Pyrolysis of cyclo*Hexanone.—Run* 19. Liquid (*b*) was substantially unchanged pyrolysand; a little water was observed, probably due to self-condensation of the ketone to *cyclo*hexylidene-*cyclo*hexanones.[16] The CO : CO_2 ratio in (*c*) was very high.

Copyrolysis of cyclo*Hexanone and Benzoic Acid.—Run* 20. Liquid (*b*) (which became red

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[29] Werner, *Ber.*, 1909, **42**, 4325; Kaufmann, King, and Huang, *Ber.*, 1942, **75**, 1201.

on standing overnight) was substantially unchanged pyrolysand; a little water was observed (cf. Run 19). The colour test [19] for acid anhydride gave a negative reaction.

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