800. *The Pyrogenesis of Ketones. Part I. The Formation of the Dipropyl Ketones.*

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Pyrolysis of sodium *iso*butyrate yields, in addition to the expected di*iso*propyl ketone, substantial quantities of *n*-propyl *iso*propyl and of di-*n*-propyl ketones, but pyrolysis of sodium *n*-butyrate and *iso*valerate does not give rise to rearranged ketonic products. It is considered that the rearranged products are the consequence of an isomeric change in the free *iso*propyl radical which is put forward as an intermediate in the reaction.

Formation of di*iso*propyl ketone, together with some *iso*butyraldehyde, was reported by Popoff (*Ber.*, 1873, **6**, 1255) amongst the products of the pyrolysis of calcium *iso*butyrate, although neither the yields nor the experimental conditions were recorded. By passing the vapours of the various fatty acids over heated manganous oxide, at 400—500°, Sabatier and Mailhe (*Compt. rend.*, 1914, **158**, 832) obtained the corresponding ketones in excellent yield they reported the formation of di*iso*propyl and di-*n*-propyl ketone from *iso*butyric and *n*-butyric acids respectively, but not the formation of rearranged products in either case. Cook, Miller, and Whitmore (*J. Amer. Chem. Soc.*, 1950, **72**, 2738), however, reported the formation of a small quantity of *n*-propyl *iso*propyl ketone in addition to di*iso*propyl ketone on passage of *iso*butyric acid vapour over heated thoria; they also reported the formation of *iso*butyl *tert.*-butyl ketone, together with smaller quantities of *tert.*-butyl ethyl and *tert.*-butyl methyl ketones, on pyrolysis of pivalic acid over this catalyst. The *iso*butyl *tert.*-butyl ketone was assumed to be formed by the occurrence of an abnormal type of Claisen condensation.

Evidence in favour of the isomerisation of the *n*-propyl to the *iso*propyl group has been claimed in several thermally promoted reactions. *E.g.*, *n*-propyl bromide vapour was converted into *iso*propyl bromide to the extent of 23% in 1 hour at 262° (Eltekoff, *Ber.*, 1873, **6**, 1258; 1875, **8**, 1244; Michael and Leupold, *Annalen*, 1911, **379**, 263); the reverse change occurred more slowly. On photochemical decomposition of di*iso*propyl ketone and trapping, by mercury, of the radicals so formed (Glazebrook and Pearson, *J.*, 1936, 1777), the product was di-*n*-propylmercury, and not di*iso*propylmercury; it was concluded that the *iso*propyl radical rearranged on combination with the mercury, and that the reverse reaction did not occur appreciably. Glazebrook and Pearson suggested that, since the α-carbon in the *n*-propyl radical is less negative than the α-carbon in the *iso*propyl radical, the isomerisation which occurs on combination with an electropositive element, *i.e.*, with an element such as a metal which would tend to donate an electron to the free radical, would be in the direction, *iso*propyl to *n*-propyl. Conversely, the combination of the *n*-propyl radical with an electronegative element (a halogen) which would tend to accept an electron from the free radical would favour the formation of *iso*propyl derivatives as reported by Eltekoff.

Electrolysis of potassium *n*- and *iso*-butyrate (Hamonet, *Compt. rend.*, 1898, **123**, 252) gave rise, in addition to propylene, which was the only hydrocarbon detected, to nearly equal proportions of *iso*propyl alcohol and the *iso*propyl ester of the appropriate acid.

These observations may be interpreted as follows :

$$\mathrm{R{\cdot}CO_2^-} \longrightarrow \mathrm{R{\cdot}} + \mathrm{CO_2} + e$$

which, when R = $\mathrm{Pr^n}$, is followed by the isomeric change $\mathrm{Pr^n{\cdot}} \longrightarrow \mathrm{Pr^i{\cdot}}$. On the assumption that the alcohol and the esters are formed by the direct attack of the free alkyl radicals on the oxygen atom with which they ultimately combine, oxygen, being an electronegative atom, should, according to Glazebrook and Pearson, favour the formation of *iso*propyl derivatives, in accordance with observation.

It has been found in the present investigation that, whereas the pyrolysis of sodium *iso*valerate and *n*-butyrate yielded almost exclusively the expected ketonic products, similar decomposition of sodium *iso*butyrate yielded a mixture of all three dipropyl ketones, in proportions dependent on the temperature (see Table).

	Ketone formed as a percentage of :		$COPr^n_2$	$COPr^nPr^i$	$COPr^i_2$
Temp.	(*a*) initial salt	(*b*) sodium carbonate formed	(% of total ketone)		
	Na *iso*butyrate.				
380°	2	100	43·1	43·7	13·2
420	15	100	45·9	41·9	12·2
460	29	35	54·2	34·3	11·5
500	80	13·3	66·3	25·8	7·9
540	98	8·0	71·8	22·9	5·3
	Na *n*-butyrate.				
440	20·2	57·7	98	—	—
	Na *iso*valerate.				
440	14·4	30·2	≮93% $COBu^i_2$		

As a consequence of isotopic tracer studies on the pyrolytic formation of acetaldehyde, Bell and Reed (*J.*, 1952, 1383) have suggested that this reaction proceeds by means of free alkyl radicals, formed thus :

$$R{\cdot}CO_2M \longrightarrow R{\cdot} + {\cdot}CO_2M$$

and that ketone formation, which always accompanies aldehyde formation, occurred as follows :

$$\begin{aligned} R{\cdot} + R{\cdot}CO_2M &\longrightarrow R_2CO + {\cdot}OM \\ OM{\cdot} + R{\cdot}CO_2M &\longrightarrow M_2CO_3 + {\cdot}R \\ \text{Termination :}\qquad 2R{\cdot} &\longrightarrow R_2 \text{ or } R' + R'', \text{ etc.} \end{aligned}$$

This mechanism, with the additional postulate of the rearrangement $Pr^{i}{\cdot} \longrightarrow Pr^{n}{\cdot}$, adequately accounts for the presence of *n*-propyl *iso*propyl ketone in the mixture, in addition to the di*iso*propyl ketone.

The evidence obtained from extensive studies of heterolytic reactions (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 601; Hughes and Ingold, *ibid.*, p. 657; Williams, *ibid.*, p. 749) supports the view that carbon atoms contained in aliphatic systems frequently become positively charged to some degree. Thus, carbon may be considered as an electropositive atom, *i.e.*, it has a tendency to donate its electrons and, by analogy with the mercury atom, is expected to favour the change $Pr^i \longrightarrow Pr^n$ which is in agreement with experiment. The rearrangement observed by Cook, Miller, and Whitmore (*loc. cit.*) can be interpreted in the same way, and the formation of *iso*butyl *tert.*-butyl ketone by decomposition of pivalic acid by assuming a change $Me_3C{\cdot} \longrightarrow Me_2CH{\cdot}CH_2{\cdot}$.

The mechanisms proposed for reactions of this type have been re-examined by Lee and Spinks (*Canad. J. Chem.*, 1953, **31**, 103) in the light of an isotopic investigation into the formation of mixed ketones by pyrolysis of mixed calcium salts. The radical rearrangement proposed above has also been criticised on the grounds that established rearrangements involving free radicals (Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438; Winstein and Seubold, *ibid.*, 1947, **69**, 2916) indicate that the primary radicals tend to rearrange to the tertiary state. However, the environment may, in accordance with the general argument discussed earlier, favour this isomerisqtion. Moreover, Lee and Spinks concluded that the radical mechanism cannot be accepted as the sole mechanism, and accordingly have proposed a heterolytic process involving the initial formation of an acyl ion $R{\cdot}C^{+}{\vdots}O$.

That a second mechanism is operative is clearly supported by Ardagh, Barbour, McClellan, and McBride's finding (*Ind. Eng. Chem.*, 1924, **16**, 1133), in the pyrolysis of calcium acetate, of traces of acetone at reaction temperatures as low as 160°. However, for the sodium salts used in our experiments, the radical mechanism is preferred. The heterolytic process does not seem well adapted to explain the formation of sodium oxalate instead of sodium carbonate in the pyrolysis of sodium formate (Merz and Weith, *Ber.*, 1882, **15**, 1507), or the preliminary results obtained in a kinetic investigation of the decomposition of sodium acetate (Reed, *J. Chem. Phys.*, 1953, **21**, 377).

In addition to the singly rearranged product, the present series of experiments yielded di-*n*-propyl ketone (not reported by Whitmore and his co-workers) in amount about equal to that of *n*-propyl *iso*propyl ketone even at the lowest temperature used. That the production of the di-*n*-propyl ketone is a consequence of a pre-equilibrium condition may be excluded, as the salt remaining after partial decomposition contained not more than 5% of the *n*-butyrate, which was about the lower limit of the methods of detection used.

This product necessitates extension of the radical theory and, in order to avoid the difficulties inherent in a mechanism involving replacement reactions, it is suggested that the second rearrangement occurs in the transition state without the rearranging radical's becoming detached.

In preliminary experiments on the pyrolysis of barium *n*-butyrate, not more than 5% of the total ketonic products were rearranged.

EXPERIMENTAL

Sodium *iso*butyrate (*ca.* 0·5 g.) was pyrolysed in a glass tube, heated by an electric furnace and connected to a U-tube cooled in liquid nitrogen, the whole being evacuated by a " Hyvac " pump. The pyrolyses were carried out at 40° intervals from 380° to 540°. The products, in each case a brown mobile liquid, were converted into the semicarbazones, which were weighed as an estimate of the total ketonic products obtained. The percentage decomposition was determined by titration of the residue. The mixed semicarbazones were separated by fractional crystallisation from the ethyl alcohol, three fractions being obtained and identified by m. p. and mixed m. p. The di*iso*propyl derivative, being the most soluble, was determined by difference. Typical results were as follows :

	$COPr^n_2$	$COPr^nPr^i$	$COPr^i_2$
M. p. of synthetic semicarbazones	133°	116°	155°
M. p. of fractions	131	116—118	152 [a]
Mixed m. p.	132	116	152

[a] Most soluble fraction, and hence the most difficult to purify.

The fractional crystallisation was tested, with good results on mixtures of the authentic compounds.

In one or two separate experiments, the residue remaining after a partial pyrolysis was examined for sodium *n*-butyrate. The m. p. (103°) of the derived anilide was not depressed on admixture with authentic *iso*butyranilide, and the *S*-benzylthiuronium derivative (m. p. 141°) showed no m. p. depression on admixture with the corresponding derivative from *iso*butyric acid. About 5% of the various *n*-butyric derivatives gave distinct m. p. depressions.

During most of the reactions, and in particular those at the higher temperatures, propylene (dibromide, b. p. 141°) was condensed in the liquid-nitrogen trap.

*Materials.—Di-*n*-propyl ketone semicarbazone.* Pentan-3-ol (from British Drug Houses Ltd.) was oxidised by potassium dichromate and sulphuric acid, and the ketone was dried ($MgSO_4$), distilled (b. p. 142—143°), and converted into the semicarbazone, m. p. 133°

Disopropyl ketone semicarbazone. When similarly prepared this had m. p. 155°.

n-*Propyl* iso*propyl ketone semicarbazone.* This was similarly prepared from 2-methylpentan-3-one (Muset, *Bull. Acad. roy Belg.*, 1906, 775) and had m. p. 116°.

Sodium iso*butyrate.* *iso*Butyric acid (from British Drug Houses Ltd.), dried ($MgSO_4$) and distilled (b. p. 152—154°), was added in 5% excess, slowly and with stirring, to an aqueous solution of " AnalaR " sodium hydroxide. The solution was evaporated to dryness (water-bath), and then heated (280°), as a melt, *in vacuo* (" Hyvac ") to remove the surplus acid. The product so obtained was neutral to phenolphthalein.

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