359. *Primary Photochemical Reactions. Part VII. Photochemical Decomposition of* iso*Valeraldehyde and Di*-n-*propyl Ketone.*

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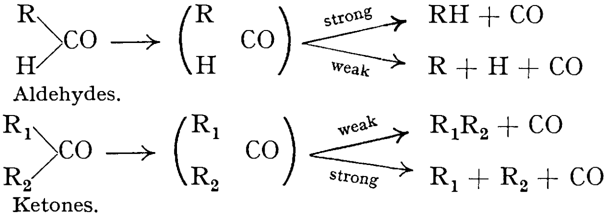
Previous studies in this series (Norrish and Kirkbride, J., 1932, 1518; Norrish, Crone, and Saltmarsh, J., 1933, 1533; 1934, 1456; Norrish and Appleyard, *ibid.*, p. 874; Saltmarsh and Norrish, this vol., p. 455) have dealt largely with the photolysis of carbonyl compounds produced by light absorbed in the generally diffuse carbonyl absorption band lying between λλ 3200 and 2000 Å. From the results obtained, and also from those of other workers with aldehydes (Leighton and Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165; 1933, **55**, 1766; de Hemptinne, *J. Phys. Radium*, 1928, **9**, 357; Bredig and Goldberger, *Z. physikal. Chem.*, 1924, **110**, 532), we have concluded that the primary photochemical act may take the form of a unimolecular elimination of carbon monoxide, which may be represented, for aldehydes and ketones alike, by the scheme



$$\begin{matrix}R\\H\end{matrix}\!>\!CO \longrightarrow \left(\begin{matrix}R\\H\end{matrix}\;CO\right) \begin{matrix}\xrightarrow{\text{strong}} RH + CO\\ \xrightarrow{\text{weak}} R + H + CO\end{matrix}$$

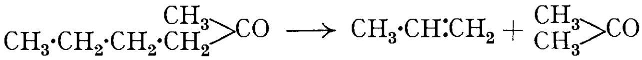
Aldehydes.

$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!CO \longrightarrow \left(\begin{matrix}R_1\\R_2\end{matrix}\;CO\right) \begin{matrix}\xrightarrow{\text{weak}} R_1R_2 + CO\\ \xrightarrow{\text{strong}} R_1 + R_2 + CO\end{matrix}$$

Ketones.

This is best visualised as a change in the multiplicity of the carbonyl group, in which a transition occurs from a triplet to a singlet state, resulting thus in the primary production of carbon monoxide. In this way it may be supposed that the bonds uniting the alkyl radicals and the hydrogen atom melt away, and two free radicals are produced at once. If the energy of the C–C bond is taken to be of the order 90 kg.-cals., and of the C–H bond as 103 kg.-cals., and the energy of the transition $CO^3\Pi \longrightarrow CO^1\Sigma$ to be 138 kg.-cals., the energy required to liberate the two free radicals at once is seen to be of the order 42 kg.-cals. for ketones and 55 kg.-cals. for aldehydes. With aldehydes, however, very few free radicals are liberated as such; instead, the hydrocarbon RH is produced before they can escape from the decomposing molecule. This is proved by the fact that very little free hydrogen is found, and by the fact that Pearson (J., 1934, 1718) was unable to isolate any free radicals by Paneth's method. It is also in accord with the recent work of Patat (*Z. physikal. Chem.*, 1934, *B*, **25**, 208), who, in the case of formaldehyde, found no free hydrogen atoms either in the region of fine structure or in that of predissociation. Nevertheless, it is now not to be doubted that some free radicals are formed in the case of aldehydes, for at high temperatures photolysis assumes the character of a chain reaction, which can only be explained in terms of free hydrogen or free methyl radicals (Leermakers, *J. Amer. Chem. Soc.*, 1934, **56**, 1899). The decomposition of ketones is analogous, except that now the two alkyl radicals mainly escape separately from the decomposing molecule. For instance, with methyl ethyl ketone, instead of only one, three hydrocarbons are found in the decomposition products in comparable quantities. It seems, therefore, that the difference between aldehydes and ketones is secondary, and we may suppose that it is bound up with the great difference in mobility between an alkyl radical and a hydrogen atom, and also with the question of steric hindrance. The following substances conform to this type of change: Ketones: acetone, methyl ethyl ketone, *cyclo*-pentanone, -hexanone, and -heptanone. Aldehydes: formaldehyde, acetaldehyde, propaldehyde, and benzaldehyde. In addition, we have shown that keten itself decomposes in a similar fashion (Norrish, Crone, and Saltmarsh, J., 1933, 357): $CH_2{:}CO \longrightarrow CH_2 + CO$. We shall describe this primary change as type I.

When studying methyl butyl ketone, Norrish and Appleyard (*loc. cit.*) found that an entirely different type of decomposition occurred, which can best be described as a species of cracking of the hydrocarbon chain:

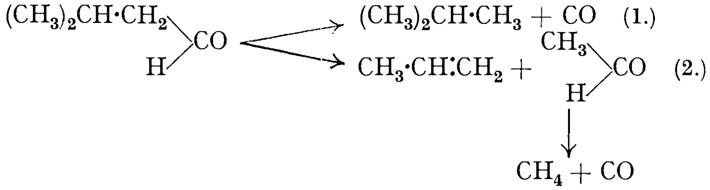


$$\begin{matrix}CH_3\\CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}\!>\!CO \longrightarrow CH_3{\cdot}CH{:}CH_2 + \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO$$

This reaction occurred in spite of the fact that the light quantum is first absorbed by the carbonyl group. There must therefore have been an exchange of energy between two parts of the molecule, and it appeared that we had here lighted upon a new type of primary change which involves the transfer of a large part of the absorbed energy (in the present instance 30—80% of the quantum) from the point of absorption to the point of reaction.

In effect, we are dealing with a type of internal sensitisation, and we shall describe this primary change as type II.

It appeared probable that such reactions would be found to be quite common with aldehydes and ketones with long chains, and the two substances named in the title were chosen in order to test this point. Our expectations have been justified : with *iso*valeraldehyde we find that 47% decomposes according to type I, and 53% according to type II, as in the following scheme :

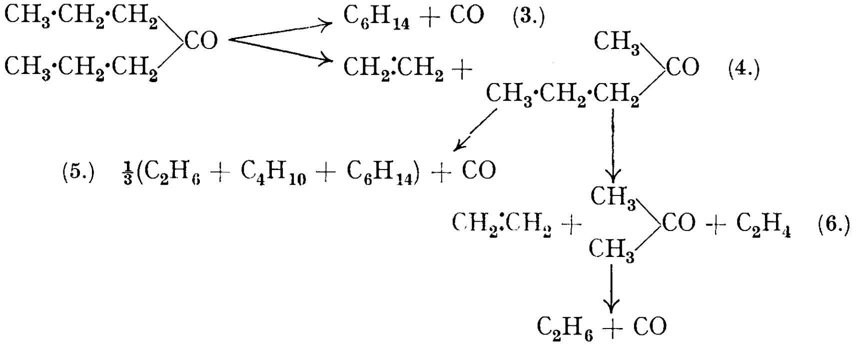


$$(CH_3)_2CH\cdot CH_2\cdot CHO \longrightarrow (CH_3)_2CH\cdot CH_3 + CO \quad (1.)$$

$$(CH_3)_2CH\cdot CH_2\cdot CHO \longrightarrow CH_3\cdot CH{:}CH_2 + CH_3\cdot CHO \quad (2.)$$

$$CH_3\cdot CHO \longrightarrow CH_4 + CO$$

With dipropyl ketone, the proportions are respectively 37% and 63% :



$$(CH_3\cdot CH_2\cdot CH_2)_2CO \longrightarrow C_6H_{14} + CO \quad (3.)$$

$$(CH_3\cdot CH_2\cdot CH_2)_2CO \longrightarrow CH_2{:}CH_2 + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3 \quad (4.)$$

$$(5.)\quad CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3 \longrightarrow \tfrac{1}{3}(C_2H_6 + C_4H_{10} + C_6H_{14}) + CO$$

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3 \longrightarrow CH_2{:}CH_2 + (CH_3)_2CO + C_2H_4 \quad (6.)$$

$$(CH_3)_2CO \longrightarrow C_2H_6 + CO$$

In all cases the break in the hydrocarbon chain occurs between the carbon atoms lying in positions α and β to the carbonyl group. Thus the energy transfer occurring is of precisely the same character as occurs with methyl butyl ketone. These results are further discussed at the end of the paper.

EXPERIMENTAL.

The methods by which the substances under investigation were irradiated, and their decomposition products identified and estimated, have already been described (Norrish and Appleyard, *loc. cit.*). In brief, they consisted in refluxing the substance in a vacuum, in a long-necked quartz flask. The vapour in the neck of the flask was never at a pressure greater than a few mm., and was subjected to irradiation from a vertical mercury lamp. The liquid was shielded from the light. The gaseous products of decomposition were collected in an evacuated globe of about 1 litre capacity. When the irradiation was complete, the products were pumped off in fractions at different temperatures ranging from that of liquid nitrogen to room temperature. The gases were collected in a gas burette, and analysed in a Bone and Wheeler apparatus. The liquids were collected in weighed tubes and weighed. Their physical properties, *i.e.*, vapour pressure, b. p., and f. p., were determined, and also their reactions with various reagents. It was usually possible to identify them with certainty.

iso*Valeraldehyde.*—The aldehyde has a considerable vapour pressure (*ca.* 4·5 cm.) at ordinary temperatures, and it was found that irradiation for 10—20 hrs. produced sufficient of the products for a satisfactory analysis. The results of two experiments are given below. Volumes are expressed in c.c. at *N.T.P.*

The analyses of fractions I, II, III were carried out in the ordinary way. The constituents of fractions II and III, *viz.*, mixtures of olefin and paraffin, were identified by explosion with oxygen (*a*) before and (*b*) after absorption of the olefin by bromine-water. None of the first three fractions contained any substance appreciably soluble in water. On shaking fraction IVA with water, there was a decrease in volume, and a considerable part dissolved; this solution was removed and found to possess aldehydic properties. It had the smell of acetaldehyde, restored the colour to Schiff's reagent, reduced Fehling's solution, and responded to the iodoform test. It was therefore a solution of acetaldehyde. The concentration of the aldehyde was estimated colorimetrically by means of Schiff's reagent, and found to agree closely with that calculated from the decrease in volume of fraction IVA when treated with water.

Fraction.	Temp. of removal.	H_2.	CH_4.	CO.	C_3H_6.	*iso*-C_4H_{10}.	CH_3·CHO.
		(i) *Irradiation for* 13 *hrs.*					
I	−196°	1·3	1·3	26·1	—	—	—
II	−130 to −135	—	—	—	9·8	2·1	—
IIIA	−100 to −105	—	—	—	8·5	5·2	—
IIIB	,, ,,	—	—	—	4·6	4·7	—
IVA	−90 to −100	—	—	—	2·7	4·9	2·0
IVB	−78	—	—	—	—	2·5	10·5
V	,,	—	—	—	—	—	7·0
	Total	1·3	1·3	26·1	25·6	19·4	19·5
		(ii) *Irradiation for* 19 *hrs.*					
I	−196	1·1	2·6	26·7	—	—	—
II	−110 to −115	—	—	—	15·5	4·3	—
III	−95 to −100	—	—	—	4·7	5·1	—
IVA	−78	—	—	—	0·9	1·9	2·5
IVB	,,	—	—	—	—	8·5	16·3
	Total	1·1	2·6	26·7	21·1	19·8	18·8

Fraction IVB when cooled in liquid air separated into two layers before solidifying. The two components were separated by fractional distillation. For this purpose the tube containing the liquid was drawn off into a capillary of the form shown in Fig. 1: it was then evacuated and sealed. The wide limb was then cooled to liquid-air temperature, and allowed to become warm, the capillary then being cooled in liquid air. By this means the top layer was distilled into the capillary, then the latter was sealed off. The f. p. and b. p. of the more volatile portion are given below, together with the data for *iso*butane for comparison:

FIG. 1.

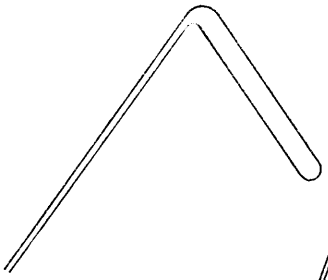
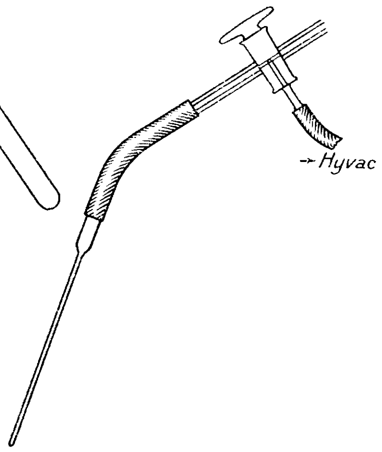


FIG. 2.



	Expt. i.		Expt. ii.	
	F. p.	B. p.	F. p.	B. p.
Liquid in capillary	−148°	−10°	−147°	− 9°
iso-C_4H_{10}	−145	−10·2	−145	−10·2

The weight of the liquid (Expt. ii) was 0·022 g., corresponding to 8·5 c.c. of gas at *N.T.P.*

The less volatile portion of fraction IVB was distilled back into the trap connected to a manometer, and its vapour pressure measured:

Temp.	V. p. of liquid, mm. Expt. i.	V. p. of liquid, mm. Expt. ii.	V. p. of acetaldehyde, mm.	Temp.	V. p. of liquid, mm. Expt. i.	V. p. of liquid, mm. Expt. ii.	V. p. of acetaldehyde, mm.
−38°	43	45	43	−28·5°	78	76	80
−33	—	58	59	−24	93	—	104
−31	68	—	67	−23	—	97	114
−30·5	—	68	69				

At the highest temperature the vapour was probably unsaturated. The vapour pressures thus corresponded closely with those of acetaldehyde : the same is true of the b. p. and f. p. as shown below :

	Expt. i.		Expt. ii.	
	F. p.	B. p.	F. p.	B. p.
Liquid from Fraction IVB	−125°	23°	−124°	23·5°
Acetaldehyde	−123·5	20·2	−123·5	20·2

The liquid was miscible with water, and the solution gave the reactions mentioned above. The less volatile portion of fraction IVB was thus identified as acetaldehyde. The weight of the liquid was 0·032 g., corresponding to 16·3 c.c. of vapour at *N.T.P.* A fifth fraction was removed in the first experiment; it was a liquid miscible with water and giving the reactions of acetaldehyde. Its f. p. and b. p. showed that it was, in fact, acetaldehyde containing a little of the original *iso*valeraldehyde as impurity (f. p. − 125°, b. p. 26°). In the second experiment no fifth fraction could be obtained possessing a vapour pressure different from that of the original aldehyde.

The results show that when *iso*valeraldehyde vapour is irradiated under the above conditions, decompositions occur according to equations (1) and (2) on p. 1506. From the equations, the volume of carbon monoxide should equal the total volume of saturated hydrocarbons, and also the volumes of aldehyde and methane should together equal that of propylene. The experimental results given fulfil these conditions satisfactorily, as shown below :

	CO, c.c.	Total saturated hydrocarbons, c.c.	Aldehyde + methane, c.c.	Propylene, c.c.
Expt. i	26·1	23·3	20·8	25·6
Expt. ii	26·7	24·2	21·4	21·1

The proportion of the total aldehyde decomposing according to equation (1) is given as 45% by Expt. i and 48% by Expt. ii.

*Di-*n*-propyl Ketone.*—The results are given below for a preliminary experiment and for a complete run; volumes are in c.c. at *N.T.P.*

Fraction.	Temp. of removal.	H_2.	CO.	C_2H_4.	C_2H_6.	C_4H_{10}.	C_6H_{14}.	$COMe_2$.	Methyl propyl ketone.
		(i) (*Preliminary*) *Irradiated for* 26 *hours.*							
I	−190°	0·3	12·1	—	—	—	—	—	—
II	−105	—	—	17·4	2·6	0·8	—	—	—
IIIA	−78	—	—	4·2	1·1	0·7	—	—	—
IIIB	,,	—	—	—	—	—	3·4	4·1	—
	Total	0·3	12·1	21·6	3·7	1·5	3·4	4·1	—
		(ii) *Irradiated for* 73 *hours.*							
I	−190	0·4	22·1	—	—	—	—	—	—
IIA	−105 to −110	—	—	29·3	4·9	2·5	—	—	—
IIB	−100 to −105	—	—	0·2	0·2	0·2	—	—	—
III	−78	—	—	—	—	—	8·8	1·5	—
IV	−35 to −40	—	—	—	—	—	3·8	—	—
V	−14	—	—	—	—	—	—	—	14·8
	Total	0·4	22·1	29·5	5·1	2·7	12·6	1·5	14·8

Fraction I in both experiments contained only carbon monoxide and hydrogen. Fraction II consisted of a mixture of olefin and paraffins; the olefin was identified in the ordinary way (described before) as ethylene, but explosion results alone could not give a complete analysis of the paraffin portion, since they were satisfied by mixtures of ethane with propane butane, etc., in suitable proportions. Physical methods showed that the paraffins present were ethane and butane. The method employed was as follows. About 5 c.c. of fraction II were treated with bromine in a gas burette to remove the ethylene, the excess of bromine being removed by potash solution. The residual paraffin occupied about 1 c.c. A short piece of narrow glass tubing, drawn out to a fine capillary which was sealed at the end, was attached to the three-way tap of the burette by pressure tubing as shown in Fig. 2. It was then exhausted, and the whole of the paraffin condensed into the capillary by cooling the latter in liquid air. When the capillary was warmed to − 80° most of the condensed gas boiled off, but a little liquid remained in the tube. Pressure–volume measurements showed that at this stage the tube contained a permanent gas. The capillary was allowed to warm up slowly, and the last trace of liquid disappeared from it at − 29°. The vapour pressure of butane at this temperature is 238 mm. According to the chemical analysis the partial pressure of butane in the tube should be *ca.* 260 mm. (the total pressure was 760 mm.). The agreement between the two figures is sufficient to identify the higher paraffin as butane.

Fraction III (Expt. ii) was a volatile liquid, which was removed in a small tube and weighed. The f. p., − 95°, suggested that it was acetone or hexane, but close examination showed that before freezing, the liquid separated into two layers, the upper one having approximately six times the volume of the lower. A mixture of acetone and hexane, in the proportion 1 : 6, was made up, and its properties compared with those of fraction III. The f. p.'s were the same, two layers were formed at − 80°, and the whole became homogeneous at about − 70° in each case. The relative volumes of the constituents were determined by distilling the liquid into a capillary, cooling to − 90°, and measuring the depths of the layers. It was possible to remove portions of the two phases separately, and perform micro-tests upon them. The substance forming the lower layer melted at − 95° and boiled at 56°. It was miscible with water, gave the iodoform test in the cold, and restored the colour to Schiff's reagent very slowly. It was thus identified as acetone (f. p. − 94·3°, b. p. 56·1°). The other constituent melted at − 95°, and boiled at 71°. It was immiscible with water, and as far as could be ascertained, inert. These properties are those of *n*-hexane, f. p. − 94·3°, b. p. 69°.

Fraction IV (Expt. ii) consisted of pure hexane, identified by its f. p. − 95°, b. p. 70°, and vapour pressure. The following table gives the v. p. at various temperatures, together with those of hexane. This fraction was immiscible with water and non-reactive.

Temp.	0·0°	−17·5°	−28·3°	−38·0°
V. p. of Fraction IV, mm.	45·0	17·5	13·5	11·5
V. p. of *n*-hexane, mm.	46·0	16·3	12·3	11·4

Fraction V was distilled off, the quartz flask being cooled in an ice–salt mixture. Distillation was allowed to proceed over-night. The liquid was again distilled from the trap, which was for this purpose cooled to − 14°, to a second smaller trap. Practically all the liquid distilled over in about 2 mins. This was removed, weighed, and examined. It was quite insoluble in water, and with concentrated sodium bisulphite solution it was completely converted into a solid addition compound. This was decomposed into the original compound by potassium hydroxide. The liquid boiled at 107°, and froze from − 75° to − 80°. These figures are close to those for methyl *n*-propyl ketone (m. p. − 77·8°, b. p. 101·7°), and consideration of the previous results of the analysis leaves no reasonable doubt that fraction V consisted of this ketone. The original di-*n*-propyl ketone does not form a bisulphite compound.

The results show that when di-*n*-propyl ketone vapour is irradiated, the decomposition occurs as shown in the scheme of equations (3, 4, 5, 6) on p. 1506. According to this scheme, the following relations should hold between the volumes of the various products :

(i) Volume of CO = total volume of saturated hydrocarbons.
(ii) Volume of C_2H_4 = volume of methyl propyl ketone obtained + (C_4H_{10}) + 2 (acetone + C_2H_6).

The experimental results satisfy these equations reasonably well, the volume of carbon monoxide being 22·1 c.c. and the total volume of saturated hydrocarbons being 20·4 c.c. The right-hand side of equation (ii) amounts to 30·7 c.c., whereas 29·5 c.c. of ethylene were obtained experimentally.

The results show that 37% of the dipropyl ketone decomposes primarily according to type I, the remainder following type II.

DISCUSSION.

The results described above show that the two substances under investigation have in each case roughly equal probabilities of decomposition by reactions of type I and type II. It seems therefore clear that the molecules must exist in two distinct states, such that the absorption of a light quantum in the first state leads to a decomposition of type I or alternatively. Just how chemically distinct these states are, cannot at present be assessed, but it is suggested that they represent merely different phases of the thermal vibrations through which the molecule periodically passes.

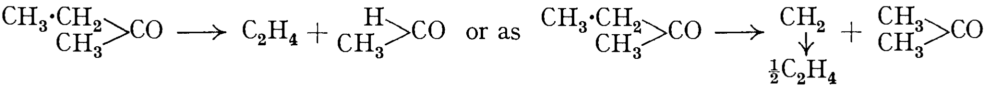
Type I decomposition of dipropyl ketone, in view of the hexane produced and of our previous results with methyl ethyl ketone (Norrish and Appleyard, *loc. cit.*), must give free radicals.*

The decomposition of *iso*valeraldehyde according to type I, on the other hand, since it gives rise almost entirely to the hydrocarbon *iso*butane and a very small proportion of free hydrogen, yields very few free radicals, as is general for aldehydes (see p. 1505). Here, as in the other cases already discussed, the hydrogen atom and free alkyl group must join up before they leave the aldehyde molecule. Nevertheless, the small amount of free hydrogen suggests that it should be possible to detect a few free butyl radicals by Paneth's method.

The alternative type of primary photodecomposition of aldehydes and ketones, which we have referred to above as type II, is now characterised with certainty. A comparison of the cases of methyl butyl ketone and *iso*valeraldehyde suggests a greater tendency for this change to occur with ketones than with aldehydes, for with the former some 90% of the whole of the ketone reacts according to type II while with the latter the partition between the two types is 40% for type I and 60% for type II. A comparison of methyl butyl ketone with dipropyl ketone further shows that the tendency for the new type of decomposition to occur increases with the length of the hydrocarbon chain.

It seems clear, from the three examples studied, that the break tends to occur in the same place relative to the carbonyl group, *viz.*, between the two carbon atoms situated in the α and the β position, and this fact suggests that there is some sort of resonance between the carbonyl group and the C–C link in this position, as a result of which the electronic energy of excitation of the former can be readily transferred wholly or in part to the latter.

The only doubtful case, so far as the above generalisation is concerned, is the decomposition of methyl ethyl ketone, a small part of which (*ca.* 5%) decomposes to give ethylene (Norrish and Appleyard, *loc. cit.*). This may be represented either as



$$\begin{matrix}CH_3{\cdot}CH_2\\ CH_3\end{matrix}\!>CO \longrightarrow C_2H_4 + \begin{matrix}H\\ CH_3\end{matrix}\!>CO \quad \text{or as} \quad \begin{matrix}CH_3{\cdot}CH_2\\ CH_3\end{matrix}\!>CO \longrightarrow \begin{matrix}CH_2\\ \downarrow\\ \tfrac{1}{2}C_2H_4\end{matrix} + \begin{matrix}CH_3\\ CH_3\end{matrix}\!>CO$$

If the reaction occurs according to the second equation, it is in accord with the generalisation made above, but if it occurs as in the first equation, then the break in the chain occurs at a different link from that concerned in the other carbonyl substances. In view of the small extent to which this change occurs, we have not yet been able to isolate either acetaldehyde or acetone to distinguish between the two possibilities.

The mechanism by which the energy may be transferred from the point of absorption to the point of reaction must at present remain obscure, and we have nothing to add to the views expressed earlier in this series (Norrish and Appleyard, *loc. cit.*). It is not to be doubted, however, that in these three examples, and others which we are now studying, a new type of primary photochemical change has been disclosed which must be of fundamental importance to the photochemistry of polyatomic molecules.

SUMMARY.

The photodecompositions of the vapours of *iso*valeraldehyde and di-*n*-propyl ketone in the light of the mercury lamp have been studied with a view to elucidate the nature of the primary change. The light absorbed corresponds to the diffuse absorption bands lying between 3000 and 2000 Å. The results of the detailed analyses of the products lead to the equations set out on p. 1506, and, taken in conjunction with the other studies of the series, confirm the existence of two types of primary photochemical change in carbonyl compounds: type I consists in an elimination of carbon monoxide to leave saturated

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* [Note added, October 15th, 1935.] At the meeting of the Society held on May 2nd (*Chem. and Ind.*, 1935, **54**, 488) it was suggested by one of us, in view of the results now described, that it should be possible to isolate the hitherto undiscovered free propyl radical from dipropyl ketone by the Paneth method as modified photochemically by Pearson. In a recent communication (*Nature*, 1935, **136**, 221). Pearson reports that he has succeeded in doing this, and he thereby provides a striking confirmation of the correctness of our conclusions.

hydrocarbons and is probably connected with a change in the multiplicity of the carbonyl group; type II involves a break between the α and the β carbon atom of the hydrocarbon chain, and results in the production of an olefin and a simpler carbonyl derivative. In this case there is an energy transfer from the chromophoric group to the point of reaction, the mechanism of which is at present not clear. It appears that the latter change occurs somewhat more readily with ketones than with aldehydes, and also that it increases in probability with the length of the hydrocarbon chain.

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