*Studies on the Chemical Decomposition of Simple Sugars. XII. Mechanism of the Acetol Formation**

By Jun'ichi HAYAMI

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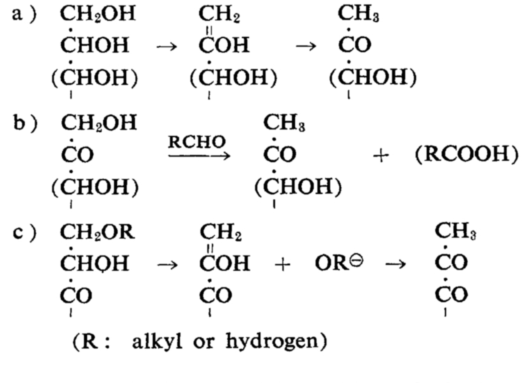
Decomposition of partially ^{14}C-labeled hexoses and of pentoses, which was reported in preceding papers[1,2] revealed the origin of every carbon atom of a resulting acetol, and the terminal carbons of a hexose and of a pentose (C-1 and C-6 of a hexose, C-1 and C-5 of a pentose) were found to be converted into the methyl carbon of acetol.

The next step is to elucidate the mechanism through which the methyl or acetyl group of acetol is formed.

As was already pointed out[2,3], triose can not be an essential intermediate in the formation of acetol from a monosaccharide. Accordingly, a direct transformation of a C_5 and of a C_6 compound is expected to take place. Generally speaking, except for hydrogenolysis and catalytic hydrogenation, examples of a direct reduction of an aldehydic or a primary carbinol group into a methyl group are scarce, especially in an aqueous reaction medium. In the present instance of acetol formation, aldose may be transformed into a ketose, and the C-1 (and C-5 or C-6) of a ketose may be converted into methyl through one of the following three possible mechanisms.



$$\begin{array}{lccccc} \text{a)} & \mathrm{CH_2OH} & & \mathrm{CH_2} & & \mathrm{CH_3} \\ & \dot{\mathrm{C}}\mathrm{HOH} & \rightarrow & \overset{\|}{\mathrm{C}}\mathrm{OH} & \rightarrow & \dot{\mathrm{C}}\mathrm{O} \\ & (\dot{\mathrm{C}}\mathrm{HOH}) & & (\dot{\mathrm{C}}\mathrm{HOH}) & & (\dot{\mathrm{C}}\mathrm{HOH}) \\ & | & & | & & | \end{array}$$

$$\begin{array}{lccccc} \text{b)} & \mathrm{CH_2OH} & & \mathrm{CH_3} & & \\ & \dot{\mathrm{C}}\mathrm{O} & \xrightarrow{\mathrm{RCHO}} & \dot{\mathrm{C}}\mathrm{O} & + & (\mathrm{RCOOH}) \\ & (\dot{\mathrm{C}}\mathrm{HOH}) & & (\dot{\mathrm{C}}\mathrm{HOH}) & & \\ & | & & | & & \end{array}$$

$$\begin{array}{lccccccc} \text{c)} & \mathrm{CH_2OR} & & \mathrm{CH_2} & & & & \mathrm{CH_3} \\ & \dot{\mathrm{C}}\mathrm{HOH} & \rightarrow & \overset{\|}{\mathrm{C}}\mathrm{OH} & + & \mathrm{OR}^{\ominus} & \rightarrow & \dot{\mathrm{C}}\mathrm{O} \\ & \dot{\mathrm{C}}\mathrm{O} & & \dot{\mathrm{C}}\mathrm{O} & & & & \dot{\mathrm{C}}\mathrm{O} \\ & | & & | & & & & | \end{array}$$

(R: alkyl or hydrogen)

They are: **a)** Simple dehydration of vic-diol, which is similar to the thermal decomposition of glycerol[4].

b) Mutual oxidation and reduction between α-ketol and aldehyde, a reaction which is analogous to the levulinic acid formation from 5-hydroxylevulinic aldehyde[5].

c) β-Hydroxy-carbonyl elimination from 3-ketose or its equivalent compound, a reaction which prevails in the reaction of carbohydrates[6,7].

Among these reactions, the possibility of **a)** can be ruled out, because sugar alcohol such as mannitol yields no acetol by the action of phosphate under decomposition condition[8].

As for **b)**, though this mechanism has been believed to operate in the formation of levulinic acid from hydroxymethylfurfural, there is opposition to this view[9], and in some cases, even an intermediate formation of 5-hydroxylevulinic aldehyde is accepted with doubt[10]. In the Teunissen's mechanism[11], 5-hydroxylevulinic aldehyde is to be converted into levulinic acid through (an intramolecular) acetal formation. This mechanism requires a specific arrangement of a hydroxyl group and an aldehydic group and, in an aqueous medium, an example of acetalformation between separated alcohols and aldehydes is yet unknown. When the above-mentioned acetal formation is to be regarded as proceeding if at all, it can be inhibited through *O*-alkylation at C-1 and/or C-6 of a hexose (C-1 and/or C-5 of a pentose), because no acetal can be produced by action of ether upon an aldehyde. Therefore, acetol formation from 1-*O*-alkylated sugars must be retarded.

As for **c)**, on the other hand, the introduction of an *O*-alkyl group on C-1 (or C-5, C-6)

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* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

Part XI, the preceding paper.

[1] R. Goto, J. Hayami, K. Kudo and S. Otani, This Bulletin, 34, 753 (1961).

[2] J. Hayami, ibid., 34, 924 (1961).

[3] R. Goto, *J. Chem. Soc. Japan*, (*Nippon Kwagaku Kwaisi*) **64**, 999, 1054, 1183 (1943); *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A20**, 197 (1937).

[4] J. U. Nef, *Ann.*, **335**, 247 (1904).

[5] F. H. Newth, "Advances in Carbohydrate Chemistry", **6**, 83 (1951), and references cited therein.

[6] J. C. Sowden, ibid., **12**, 36 (1957).

[7] R. L. Whistler and J. N. BeMiller, ibid., **13**, 289 (1958).

[8] R. Goto, unpublished work.

[9] A. P. Dunlop and F. N. Peters, "Furans", Reinhold, New York (1953), p. 648.

[10] F. Leger and H. Hibbert, *Can. J. Research*, **16B**, 68 (1938).

[11] H. P. Teunissen, *Rec. trav. chim.*, **50**, 1 (1930); R. Pummerer and W. Gump, *Ber.*, **56**, 999 (1923); R. Pummerer, O. Guyot and L. Birkofer, ibid., **68**, 480 (1935).

may facilitate the β-hydroxy-carbonyl elimination from 3-ketose to convert the C–1 into methyl group; thus the formation of acetol from the sugar may be accelerated.

In the present work, 1-*O*-methyl-D-fructose (I), 3-*O*-methyl-D-glucose (II), and 6-*O*-methyl-D-glucose (III) were decomposed to decide which of these two cases actully occurs, and combining the results with those of tracer experiments reported earlier, a general mechanism of acetol formation was made clear.

Experimental

Methylated Sugars.—1-*O*-Methyl-D-fructose[12] was synthesized from sucrose through di-*O*-isopropylidene fructose, and 3-*O*-metyl-D-glucose[12] was synthesized from glucose through di-*O*-isopropylidene-D-glucose in the usual way. 6-*O*-Methyl-D-glucose was synthesized through 1,2-*O*-isopropylidene-6-*O*-tosyl-D-glucose and 1,2-*O*-isopropylidene-5,6-epoxy-D-glucose according to the combination of Reist's method[13] with Ohle's method[14].

Decomposition of Methylated Sugars.—A solution of 5.4 g. of 1-*O*-methyl-D-fructose or 6-*O*-methyl-D-glucose in 200 ml. of concentrated potassium hydrogen phosphate buffer (40%, pH 6.7), was heated and distilled in the usual way which was described earlier in a paper[1] (Part X) of this series. In the case of 3-*O*-methyl-glucose, 10.8 g. of the sugar was decomposed in the same way. In the reference experiment, each 5 g. or 10 g. of parent sugar was decomposed.

Estimation of Acetol in a Distillate[15].—To 10 ml. of the distillate were added 10 ml. of N/10 KI-I_2 solution and 10 ml. of 10% potassium hydroxide solution. After 30 min., the mixture was acidified with 8 ml. of 15% hydrochloric acid, and liberated iodine was titrated with N/10 $Na_2S_2O_3$ standard solution. One milliliter of N/10 KI-I_2 solution corresponds to 0.73 mg. of acetol. The amount of acetol was plotted against time, thus distillation curves were given for each sugar and derivative respectively (Figs. 1—3).

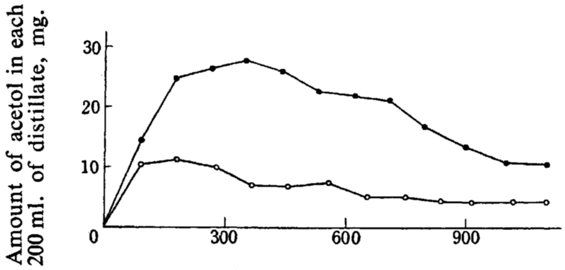

Fig. 1. Acetol formation from 3-*O*-methyl-D-glucose (—○—) (10.8 g.) and from D-glucose (—●—) (10.0 g.) in 200 ml. of potassium hydrogen phosphate buffer solution (ca. 40%, pH 6.7); 200 ml. of distillate was collected for each 90 min. The amount of acetol was determined by iodometric titration, though 3-*O*-methyl-D-glucose actually gave no acetol (also refer to Table I).

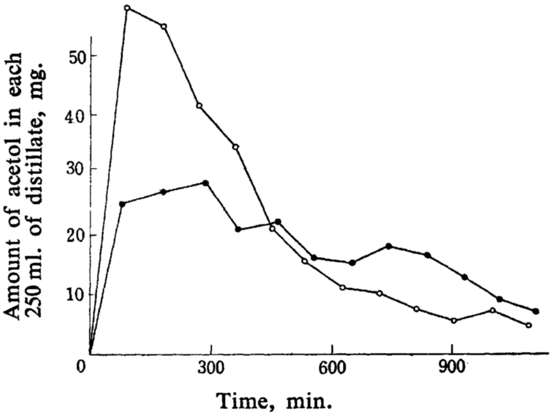

Fig. 2. Acetol formation from 1-*O*-methyl-D-fructose (—○—) (5.4 g.) and from D-fructose (—●—) (5.0 g.) in 200 ml. of potassium hydrogen phosphate buffer solution (ca. 40%, pH 6.7); 250 ml. of distillate was collected for each 90 min. The amount of acetol was determined by iodometric titration.

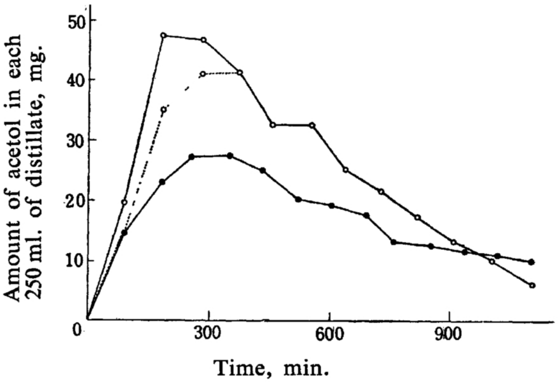

Fig. 3. Acetol formation from 6-*O*-methyl-D-glucose (—○—) (5.4 g.) and from D-glucose (—●—) (5.0 g.) in 200 ml. of potassium hydrogen phosphate buffer solution (ca. 40%, pH 6.7); 250 ml. of distillate was collected for each 90 min. The amount of acetol was determined by iodemetric titration (solid line) and corrected by UV. absorption measurement (dotted line).

Every distillate was collected, and acetol in the distillate was treated with 5-fold equivalents of semicarbazide hydrochloride and of sodium acetate. The mixture was heated over a boiling water bath for 30 min., cooled and concentrated under reduced pressure. Acetol semicarbazone was separated and repeatedly recrystallized from hot water to give colorless needles. Melting point and mixed melting point 199~200°C.

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[12] W. L. Glen, *J. Chem. Soc.*, **1951**, 2568.
[13] E. J. Reist et al., *J. Org. Chem.*, **23**, 1753 (1958).
[14] H. Ohle and L. Vargha, *Ber.*, **62**, 2435 (1929).
[15] R. Nodzu, This Bulletin, **10**, 122 (1935).

TABLE I. ACETOL FORMATION FROM PARTIALLY *O*-METHYLATED HEXOSES

Sample		Distillate ml.	Acetol* mg.	Acetol semi-carbazone mg.
	3-*O*-Methyl-D-glucose			
3-*O*-Methyl-D-glucose	10.8 g.	2400	79.3	0
Glucose	10.0 g.	2400	251.6	70
	1-*O*-Methyl-D-fructose			
1-*O*-Methyl-D-fructose	5.4 g.	3000	269.8	83
Fructose	5.0 g.	3000	218.2	65
	6-*O*-Methyl-D-glucose			
6-*O*-Methyl-D-glucose	5.4 g.	3000	322.6 (288.9)**	100
Glucose	5.0 g.	3000	223.7	60

* Calculated from the titration of iodine consuming substances (assuming only acetol was present).

** Corrected value from the peak hight of UV absorption spectrum.

Results and Discussion

The results which are shown in the above table and figures can be expressed as follows.

i) In the case of 3-*O*-methyl-D-glucose(II), the formation of iodine-consuming substances were depressed in a marked degree. Acetol semicarbazone could not be isolated, and the ultraviolet absorption spectrum of the distillate did not show the characteristics[16] of acetol. Thus, the introduction of 3-*O*-methyl group was shown to hinder the formation of acetol from glucose.

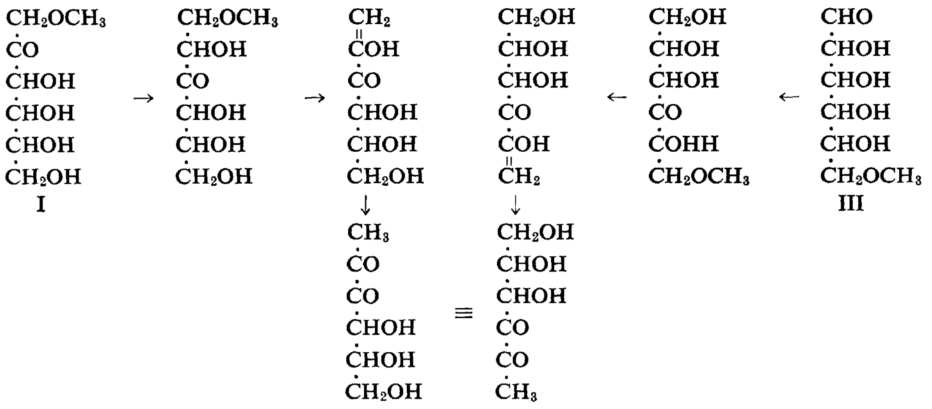
ii) On the other hand, remarkably rapid formation of acetol from 1-*O*-methyl-D-fructose (I) was observed; the rate of formation was about twice that from the parent fructose. Acetol semicarbazone was actually isolated from the decomposition distillate of 1-*O*-methyl-D-fructose as well as from that of D-fructose.

iii) 6-*O*-Methyl-D-glucose(III) also showed enhanced rate of acetol formation, and the amount of acetol was even greater than that of glucose. The amount of acetol estimated by iodometric titration was corrected by the peak height of ultraviolet absorption spectrum and was shown in Fig. 3 (dotted line). These facts might mean that the introduction of 6-*O*-methyl group would raise the amount of acetol formation but not the rate of formation.

It is well known[6,7] that *O*-alkylation of the hydroxyl group located at the β-position to the carbonyl group always facilitates an elimination of alkoxyl anion more (compared with that of hydroxyl anion from parent compound).

In the present instance, the formation of acetol was accelerated by introduction of 1-*O*-methyl (and 6-*O*-metyl) group into hexose. These facts mean that β-hydroxy-carbonyl elimination from 3- (and/or 4-) ketohexose is operating on an essential pathway of this reaction, and that oxidation-reduction mechanism (the pathway b cited above) do not play an important role.

These processes may be written as follows:



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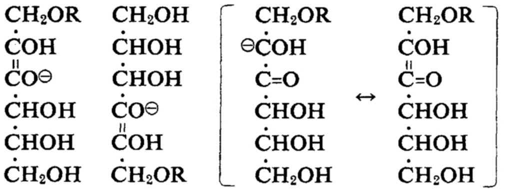
[16] R. Nodzu and R. Goto, ibid. 11, 281 (1936).

3- or 4-ketohexose in the above scheme may actually be a hexose-2, 3- or 3, 4-enediol. According to Isbell[17] (IVa, b) and to Whistler[7] (IVc), a direct intermediate from which alkoxyl anion is eliminated may be an enediolate anion.

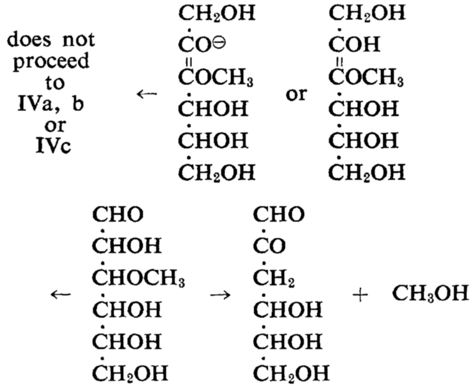


$$\begin{array}{llcccc}
\mathrm{CH_2OR} & \mathrm{CH_2OH} & \left[\begin{array}{l}\mathrm{CH_2OR}\\ {}^{\ominus}\mathrm{COH}\\ \mathrm{C{=}O}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}\right. & \leftrightarrow & \left.\begin{array}{l}\mathrm{CH_2OR}\\ \mathrm{COH}\\ \overset{\|}{\mathrm{C}}\mathrm{{=}O}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}\right] \\
\mathrm{COH} & \mathrm{CHOH} &&&\\
\overset{\|}{\mathrm{C}}\mathrm{O}^{\ominus} & \mathrm{CHOH} &&&\\
\mathrm{CHOH} & \mathrm{CO}^{\ominus} &&&\\
\mathrm{CHOH} & \overset{\|}{\mathrm{C}}\mathrm{OH} &&&\\
\mathrm{CH_2OH} & \mathrm{CH_2OR} &&&
\end{array}$$

IVa IVb IVc

These enediol or enediolate are quite probable intermediates in the transformation of sugars[18], in fact Sowden[19] offered a solid experimental evidence of the existence and of the important role of the hexose-3, 4-enediols in the isomerization of hexose.

With above illustrations, the behavior of 3-*O*-methyl-D-glucose (II) can be well understood in the following way.

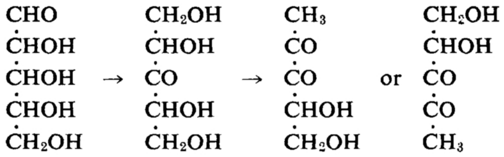


$$\begin{array}{l}
\text{does not proceed to IVa, b or IVc} \leftarrow \begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{CO}^{\ominus}\\ \overset{\|}{\mathrm{C}}\mathrm{OCH_3}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \text{ or } \begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{COH}\\ \overset{\|}{\mathrm{C}}\mathrm{OCH_3}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}\\
\leftarrow \begin{array}{l}\mathrm{CHO}\\ \mathrm{CHOH}\\ \mathrm{CHOCH_3}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CHO}\\ \mathrm{CO}\\ \mathrm{CH_2}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} + \mathrm{CH_3OH}
\end{array}$$

II V

First, under the influence of carbonyl group located at C-1, the elimination of $OR^{\ominus}$ ($OCH_3^{\ominus}$) anion from 3-position (β- to the carbonyl group) is facilitated. Thus, 3-deoxyosone (V) (or its enol form) may be formed, and make it difficult to transform the C-1 into methyl group. Second, 3-*O*-alkyl group hinders the enol traverse down the carbon chain to form IVa, b or IVc, which is required for formation of acetol.

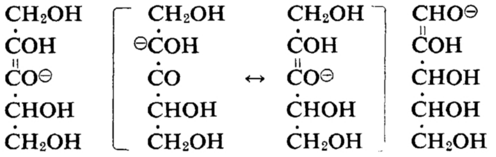
When the above illustrations are applied to a pentose, β-hydroxy-carbonyl elimination from a 3-ketose will proceed as follows:



$$\begin{array}{l}\mathrm{CHO}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{CHOH}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \text{ or } \begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{CHOH}\\ \mathrm{CO}\\ \mathrm{CO}\\ \mathrm{CH_3}\end{array}$$

VI

The actual intermediates from which hydroxyl anion is eliminated may be an enediolate anion VIIa or VIIb. These endiolate anions would be derived either directly from VI or from VIII by prototropy.



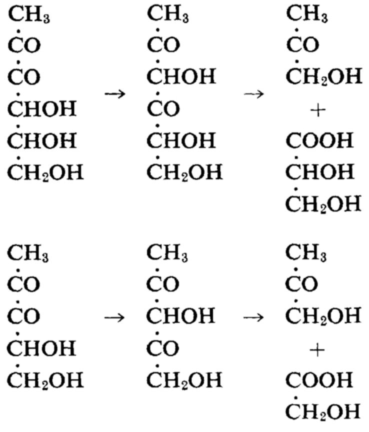
$$\begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{COH}\\ \overset{\|}{\mathrm{C}}\mathrm{O}^{\ominus}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \quad \left[\begin{array}{l}\mathrm{CH_2OH}\\ {}^{\ominus}\mathrm{COH}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \leftrightarrow \begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{COH}\\ \overset{\|}{\mathrm{C}}\mathrm{O}^{\ominus}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}\right] \quad \begin{array}{l}\mathrm{CHO}^{\ominus}\\ \overset{\|}{\mathrm{C}}\mathrm{OH}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}$$

VIIa VIIb VIII

Examination of these formulae of the intermediate shows that β-hydroxy-carbonyl elimination may take place either at C-1 or at C-5 with equal chance. Or strictly speaking, contribution of the lower C_3 part of the pentose may be greater than that of the hexose. In other words, the intermediate for formation of acetol from a pentose might have a high degree of symmetry. This was proved to be the case as was described in Part XI of this series of papers[2].

From the above discussion, it should be clearly evident that β-hydroxy-carbonyl elimination from 3-ketose (and/or from 4-ketose in the case of hexose) takes place as an essential part of the general mechanism of the acetol formation.

Fate of the α-diketones, formed by β-hydroxy-carbonyl elimination, is supposed as follows:



$$\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CH_2OH}\\ +\\ \mathrm{COOH}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array}$$

$$\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CHOH}\\ \mathrm{CO}\\ \mathrm{CH_2OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{CH_2OH}\\ +\\ \mathrm{COOH}\\ \mathrm{CH_2OH}\end{array}$$

i) In the pH region where formation of acetol is to be observed (pH 3~11), these

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[17] H. S. Isbell, *J. Research NBS.*, **32**, 45 (1944); and also refer to the excellent reviews by Sowden (loc. cit.).

[18] J. C. Speck, Jr., "Advances in Carbohydrate Chemistry", Vol. 13, 63 (1958).

[19] J. C. Sowden, and R. R. Thompson, *J. Am. Chem. Soc.*, **80**, 1435 (1958).

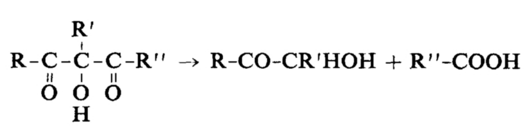
α-diketones do not rearrange[*1] by a benzilic acid type of reaction to yield saccharinic acids.

ii) These α-diketones would be isomerized into β-diketones[*2] (diacylcarbinols), and then hydrolytically cleft into α-ketol and acid.

iii) Among these processes, no skeletal rearrangement of the C_6 and of the C_5 chain would take place, and this third supposition had its evidence as already described in the Part X of this series of the paper[1)].

Isomerization of the α-diketone into β-diketone (diacylcarbinol), is one of the general transformations of ketol, and an example by Hesse and Stahl[20)] illustrates a quite similar reaction of the isomerization of pentane-2, 3-dione-4-ol to diacetyl carbinol.

The resulting diacylcarbinol is quite reactive and is facile to be cleft hydrolytically according to the following general formula[21-24)].

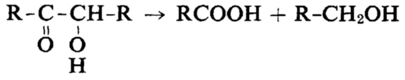


$$\underset{\overset{\|}{O}}{R\text{-}C}\text{-}\overset{\overset{R'}{|}}{\underset{\underset{H}{\overset{|}{O}}}{C}}\text{-}\underset{\overset{\|}{O}}{C}\text{-}R'' \rightarrow R\text{-}CO\text{-}CR'HOH + R''\text{-}COOH$$

and $R''\text{-}CO\text{-}CR'HOH + R\text{-}COOH$

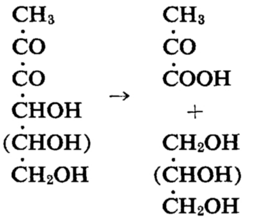
$R=R''=Et,\ R'=Me$	(House[21)])
$R=R'=R''=Me$	(Juni and Heym[22)])
$R=R''=Me,\ R'=H$	(Combes[23)])
$R=R''=Ph,\ R'=H$	(Karrer[24)])

This hydrolytic cleavage can be taken as an extreme case of an acyloin cleavage[25)] which is shown as follows:



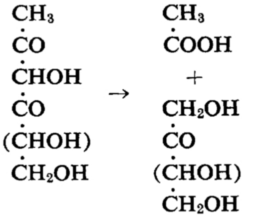
$$R\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\underset{H}{\overset{|}{O}}}{CH}\text{-}R \rightarrow RCOOH + R\text{-}CH_2OH$$

These hydrolytic cleavages may take part in constituting the side reactions in the following way:



$$\begin{array}{l} CH_3 \\ \dot{C}O \\ \dot{C}O \\ \dot{C}HOH \\ (\dot{C}HOH) \\ \dot{C}H_2OH \end{array} \rightarrow \begin{array}{c} CH_3 \\ \dot{C}O \\ \dot{C}OOH \\ + \\ CH_2OH \\ (\dot{C}HOH) \\ \dot{C}H_2OH \end{array}$$

(pyruvic acid formation)



$$\begin{array}{l} CH_3 \\ \dot{C}O \\ \dot{C}HOH \\ \dot{C}O \\ (\dot{C}HOH) \\ \dot{C}H_2OH \end{array} \rightarrow \begin{array}{c} CH_3 \\ \dot{C}OOH \\ + \\ CH_2OH \\ \dot{C}O \\ (\dot{C}HOH) \\ \dot{C}H_2OH \end{array}$$

The accompanying formation of pyruvic acid with acetol is already referred to[26)]. But the origins and the mode of the formation of the other minor products still remain to be resolved.

As for the role of hydrogen phosphate in the formation of acetol, the following inferences seem to be possible: a) acting as an effective buffer solution keeping the pH of the solution nearly constant. Without these buffers, the pH of the solution decreases remarkably to about 3[*3], b) acting as a base as well as acting as an acid, thus promoting the transformation of sugars[18)] and promoting elimination of $OH^{\ominus}$ anion and of a proton from some intermediates, c) raising the reaction temperature and raising the dielectric constant of the solution to facilitate the ionic processes. These inferences will be examined in detail in future studies.

Essential features of the formation of acetol can be summarized in the following sequences and are expressed in the scheme shown below.

I) Isomerization of monosaccharides to produce 3-ketoses (and/or 4-ketose in the case of hexose) or their equivalent intermediates.

II) β-Hydroxy-carbonyl elimination from the 3-ketose to yield methyl-α-diketones.

III) Hydrolytic cleavage of β-diketone (diacylcarbinol) produced by the isomerization of methyl-α-diketone.

[*1] A benzilic acid type of rearrangement proceeds with a rate proportional to concentration of OH^- ion. In addition, in one of the most simple examples of the rearrangement, methylglyoxal produces lactic acid (cf. J. C. Sowden and E. K. Pohlen, *J. Am. Chem. Soc.*, **80**, 242 (1958).) only in alkaline solution that is stronger than N/100 NaOH (about pH 12) (cf. V. Prey et al., *Monatsh.*, **85**, 1186 (1954)).

[*2] Further β-hydroxy-carbonyl elimination from this β-diketone might result. In the case of hexose, $CH_3COCO\cdot CHOHCOCH_3$ (Nodzu's acetylformoin) may result by elimination reaction. As was reported earlier, Nodzu confirmed the formation of acetol and of pyruvic acid by a (hydrolytic) cleavage of this compound.
In a sense, the present work appears to offer a theoretical and experimental evidence for part of Nodzu's mechanism, and the present author will not exclude the possibility that in the case of hexose Nodzu's mechanism operates as a minor pathway of the acetol formation.

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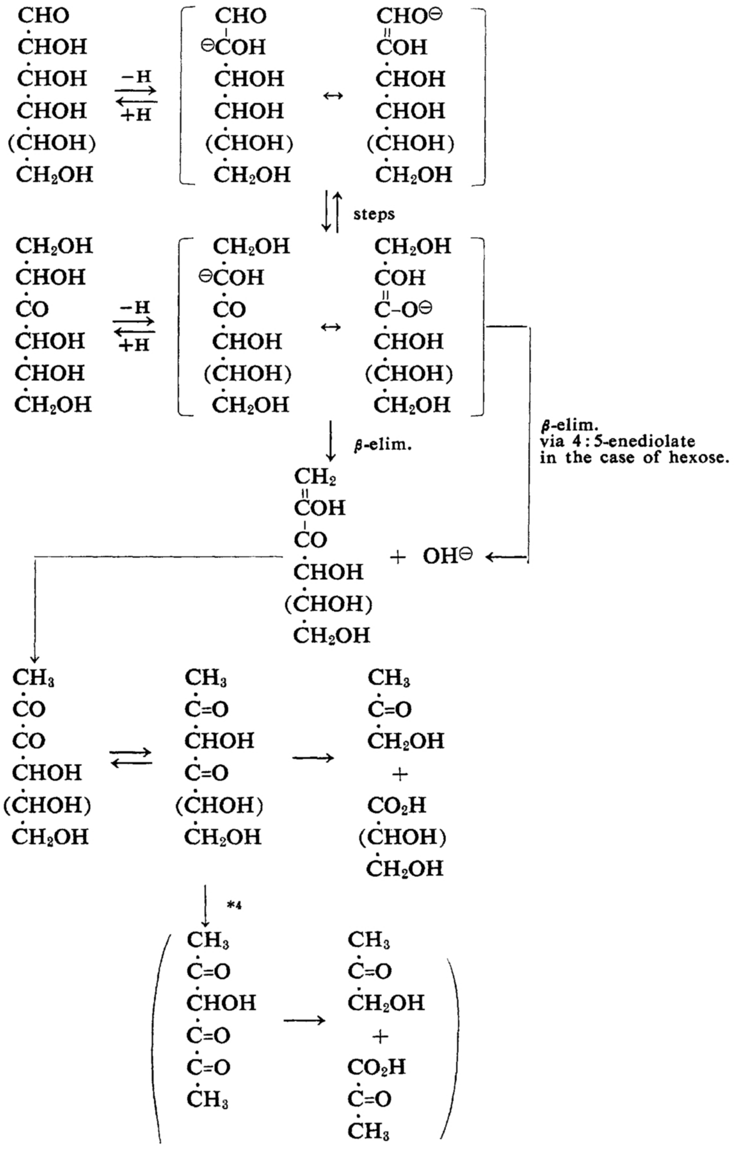
24) P. Karrer et al., *Helv. Chim. Acta*, **33**, 1711 (1950); **34**, 1014, 1498 (1952).

25) D. B. Sharp and E. L. Miller, *J. Am. Chem. Soc.*, **74**, 5643 (1952).

26) R. Nodzu et al., *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A20**, 197 (1937).

[*3] Formation of acetol is to be seen at pH 3~11 with an increased yield with the increase in pH. Also refer to R. Montgomery and L. F. Wiggins, *J. Soc. Chem. Ind.*, **66**, 31 (1947); M. L. Wolfrom and W. L. Shilling, *J. Am. Chem. Soc.*, **73**, 3557 (1951).



The formation of acetol constitutes one example of a new combination of the two basic reactions of carbohydrate chemistry—the transformation (van Eckenstein reaction) and the benzilic acid type of rearrangement. While no transformation and no rearrangement occur in the furfural formation, saccharinic acid formation requires both the transformation and the rearrangement, and metasaccharinic acid formation requires no transformation but requires rearrangement. In the present case, the transformation is not followed by any rearrangement.

In the present instance, needless to add, much possibility of another pathway which competes with the acetol formation is expected though the nature of such a competing reaction is entirely unknown.

Study on the individual reactions involved in the present instances is in progress and will be reported later.

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Institute of Chemistry
Faculty of Science
Kyoto University
Sakyo-ku, Kyoto

[*4] in the case of hexose.