



## Studies on Higher Aliphatic Aldehydes and Related Compounds

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# Studies on Higher Aliphatic Aldehydes and Related Compounds

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若山 誠治：  
高級脂肪族アルデヒド及び関連化合物の研究

## I Introduction

As a preliminary experiment in a study intended to establish a new method of preparing aliphatic aldehydes, the acetylation of octanal was investigated.

The acetylation of octanal was accomplished with acetic anhydride in the presence of an acid catalyst such as sulfuric acid, producing only diacetate, but no monoacetate.

At the beginning of the reaction octanal (liquid) was solidified by polymerization and then liquidified, producing octanal diacetate. As the intermediate solid is an octanal trimer, this change of phase can be illustrated satisfactorily, considering the equilibrium between octanal and its trimer, as is described later (Chapter II).

In literature\* abnormal data have been described in the case of dodecanal. Zaal\*\* stated that there exist two forms of dodecanal, melting at 11.1° and 44.5° respectively.

On conservation of the former it changed into the latter and precipitated. He thus concluded without confirmation these two forms would be in Keto-enol tautomerism and dodecanal melting at 44.5° would be the enol-form.

These phenomena have now been elucidated by investigation on dodecanal prepared by dry distillation of a mixture of barium-laurate and barium-formate. As in the case of octanal an equilibrium between the monomer and the trimer was shown. Furthermore, the molecular compound of dodecanal and dodecanol, which was first found by Zaal, was discussed. (Chapter III)

A new method for the preparation of aliphatic  $\alpha\beta$ -unsaturated aldehyde having a straight carbon chain was established.

(Chapter IV).

By this method five new  $\alpha\beta$ -unsaturated aldehydes and twenty six intermediates were synthesized and their properties were elucidated (Chapters IV and V).

\* H. Meyer, nachw u. Bestim. Org. Verb.S. (1933)

Guenther, Essentialoils Vol. p. (119)

\*\* B. Zaal, J. Prak. Chem. 132 169 (1931)

## II Studies on Octanal\*

The formation of enol acetate of aliphatic aldehydes has been known from a good many years ago. Semmler<sup>1)</sup> obtained octanal acetate and octanal diacetate by refluxing octanal with acetic anhydride in the presence of anhydrous sodium acetate for an hour; he stated that in this reaction at first octanal diacetate would be yielded, from which octanal acetate would be converted by heat decomposition.

The acetylation of octanal is accomplished using ferric chloride, sulfuric acid, etc. as catalyser<sup>2)</sup>, producing solely diacetate, but no monoacetate.

At the beginning of the acetylation octanal (liquid) solidified, and then liquidified, producing octanal diacetate.

As the intermediate solid is an octanal trimer (paraoctanal) the change of phase will be illustrated as follows :

The conversion from octanal to paraoctanal is reversible and proceeds quickly at a low temperature, so at the beginning of the reaction equilibrium is soon attained, precipitating paraoctanal, mp 33.5~34°.

However when the acetylation of octanal in the equilibrium mixture proceeds and produces octanal diacetate, octanal becomes deficient, so the equilibrium shifts to octanal.

Repeating this, finally all the precipitated solid liquidifies and octanal diacetate results.

The decomposition of octanal diacetate to octanal was accomplished with difficulty as described later in the experimental parts.

Diacetals of octanal with methyl-, ethyl-, butyl- and isoamyl-alcohol were synthesized in the same way from octanal as well as paraoctanal, on heating with alcohol which contains one percent hydrogen chloride.

The conversion of octanal to paraoctanal and the regeneration of octanal from paraoctanal are easily accomplished in the presence of sulfuric acid, so paraoctanal is a convenient form in which store potential octanal.

### Experimental

#### Synthesis of Octanal<sup>3)</sup>

Copper, used as catalyst, was prepared through hydrogenation of cupric oxide attached on pumice which was placed in a reaction tube of glass at 300° in a stream of hydrogen for 6 hours. Cupric oxide had been precipitated by mixing copper sulfate (1 mole solution) with N-sodium hydroxide and washed with hot water until washings were neutral to litmus. The yields of intermediates and final product were as follows :

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\* Already published in Japanese  
J. Chem. Soc. Japan. 72, 275 (1951)

1) Semmler, Ber. 42 1161 (1909).

2) Knoevenagel, Ann. 402 119 (1914).

Started from 180g of octanal (80°/6mm), reaction mixture 175.5g, sodium bisulfite addition compound 122g, regenerated aldehyde 60g. Through rectification 45.7g of octanal (76~78°/23mm) was obtained.

#### Synthesis of Octanal Diacetate

Acetic anhydride (6g) containing ferric chloride (0.2g) was added to octanal (5g) under cooling (ice). Octanal was solidified\* at first upon the addition of 1~2 drops of acetic anhydride (rapid elevation of the reaction temperature). After all acetic anhydride was added, the reaction mixture was stood for 3 hours at room temperature with skaking,\*\* decomposed with sodium carbonate (2n,) extracted with ether, washed with water, dried over anhydrous sodium sulfate and the ether removed. Yielded 8.9g, fractionated at 8mm.,

Distillate (1) 115~122° 0.8g  
 " (2) 122~123° 7.0g                      7.8g (86.7%)

Distillate (2) distilled at 111° by refractionation at 3mm. Found: C, 62.42, H, 9.85, Calcd. for C<sub>12</sub> H<sub>22</sub> O<sub>4</sub>: C, 62.60, H, 9.57%.

No monoacetate (90~94°/10mm., Semmler) was yielded.

When octanal diacetate (2g) was heated under reflux for one hour, odor of acetic acid was recognized in high concentration, indicating the decomposition of the diacetate. Fractionated at 10mm.,

Distillate (1) 101~130° 0.45g  
 " (2) 130~133°~136° 1.0g  
 " (3) residue 0.3g

In this case also no octanal monoacetate was obtained. Perhaps the produced monoacetate had been polymerized.

Semmler's experiments<sup>1)</sup> were repeated. Started from 30.8g octanal, 38.5g of the reaction mixture was obtained. Fractionated under reduced pressure (10mm.),

Distillate (1) 60~65~80° 11.5g  
 " (2) 80~90~95~120. 12.2g  
 " (3) 120~130~134° 8.7g

Distillate (3) distilled at 109~111° by refractionation at 3mm. Judging from the boiling point, distillate (1) corresponds to unconverted octanal, distillate (2) to octanal monoacetate and distillate (3) to octanal diacetate.

#### Decomposition of octanal diacetate

Decomposition of octanal diacetate with hydrochloric acid, sulfuric acid and sodium carbonate was tried.<sup>4)</sup> Though every decomposition tried had not yet been completed,

3) Pickard, J. Chem. Soc. 99 56 (1911)

\* The solid separated, melted at 33.5~34° after recrystallization from acetone.

\*\* The solid disappeared in about 10 minutes, whereas the reaction temperature sank from 23° to the room temperature (10°) in about 15 minutes.

the best result was :

After a mixture of octanal diacetate (3g), 15% sulfuric acid (6g) and ethanol (6g) was refluxed for one hour, the reaction mixture was diluted with water, extracted with ether, washed with water, dried and the ether removed. Yielded 2.45g, fractionated at 10mm.

Distillate (1) 58~65\*\* 1.0g  
" (2) 65~90° 0.75g

Distillate (1) reduced silver nitrate, yielding a silver mirror. Oxim melted at 59°, identified as octanal oxim.

#### Octanal trimer

The compound melting at 33.5~34° above described was almost quantitatively yielded from octanal and a small respective amount of sulfuric acid, hydrochloric acid, ferric chloride, stannous chloride, zinc chloride and aluminium chloride under cooling (ice). It melted at 33.5~34° after recrystallization from acetone. Found: C, 74.85, H, 12.70, Mol. wt. (Cryoscopic, benzene) 387. Calcd. for C<sub>24</sub> H<sub>48</sub> O<sub>3</sub>: C, 74.93, H, 12.70%, Mol. wt. 384.

Negative for the silver mirror test of ammoniacal silver nitrate and Schiff's aldehyde-reagent.

That is to say, it is an octanal trimer\*\* and would have a similar configuration with paraldehyde.

Infrared spectrum in CCl<sub>4</sub>: 2940, 2860, 1465, 1367, 1188, 1123cm<sup>-1</sup>: C=O-band (1710cm<sup>-1</sup>) disappears and ether C-O band (1123cm<sup>-1</sup>) appears.

Depolymerization of paraoctanal is accomplished by addition of a trace of an acid catalyst and distillation. For example by distillation of paraoctanal (2g) with a trace of sulfuric acid, octanal was distilled at 42~43° (yield, 1.65g. oxim, mp. 59°). The depolymerization of paraoctanal stored for 6 months was accomplished in the same manner. Paraoctanal is easily soluble in benzene and carbon tetrachloride, soluble in ether, ethyl acetate and acetone, sparingly soluble in ethanol.

#### Syntheses of acetals

Alcohol (10g) containing 1% hydrogen chloride was added to paraoctanal (2g) and allowed to stand at 40° for 2 hours with stirring. The reaction mixture was poured into a large amount of water, extracted with ether, washed with water, dried and the ether removed. The residue was distilled under diminished pressure. In the case of butyl- and isoamyl-alcohol the reaction mixture was washed with water, dried and distilled under diminished pressure.

\* The wide range of boiling point may be due to the octanal diethyl acetal produced.

4) Houben-Weyl, Meth. Org. Chem. Bd. 3 S. 161 (1923)

\*\* The octanal trimer had been unknown. It should be called "paraoctanal".

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Name  $\text{CH}_3$   $(\text{CH}_2)_6$   $\text{CH}$   $(\text{OR})_2$ , boiling point ( $^\circ/\text{mm}$ ), specific gravity ( $d_4^{20}$ ), refractive index ( $n_D^{20}$ ) and yield (% by theory) of synthesized acetals are as follows :

R	o. p.	$d_4^{20}$	$n_D^{20}$	Yield
methyl-	88~89 $^\circ$ /20	0.8493	1.4176	83
ethyl-	115~117 $^\circ$ /20	0.8434	1.4187	85
n-propyl-*	136~138 $^\circ$ /20	0.8369	1.4235	94
n-butyl-	147~150 $^\circ$ /10	0.8377	1.4286	85
isoamyl-*	153~156 $^\circ$ /10	0.8369	1.4305	56

\* unknown

Analyses :

Octanal di-n-propylacetal

Found : C, 72.86, H, 13.25 Calcd. for  $\text{C}_{14}\text{H}_{30}\text{O}_2$  : C, 72.97 H, 13.13%.

Octanal iso amyl acetal

Found C, 75.22, H, 13.47, Calcd. for  $\text{C}_{18}\text{H}_{38}\text{O}_2$  : C, 75.45, H, 13.38%.

By Ueno<sup>5)</sup> acetals of octanal (methyl-, ethyl-, butyl-) were prepared by refluxing octanal with alcohols containing, 1% hydrogen chloride and found to have properties available in making perfumery as an essence and an imitation.

That their yields, however, were too low, may probably be due to decomposition and polymerization resulting from long standing in high temperature

The reaction was carried out at 40 $^\circ$ , when diacetal was obtained in a good yield after a short time.

Ethanol (7.5g) containing, 1% hydrogen chloride was added to octanal (1.5g), allowed to stand for 2 hours at 40 $^\circ$  with stirring, diluted with a large amount of water and extracted with ether. The ether extract was washed with water, dried and the ether removed. Yielded 3.2g, fractionated at 20mm.,

Distillate (1) 82~113 $^\circ$  0.5g

" (2) 113~115~116 $^\circ$  2.0g

Distillate (2) was identical with octanal diethyl acetal prepared from paraoctanal in its properties (b. p.,  $d_4^{20}$ ,  $n_D^{20}$ ).

Found : C, 71.15, H, 12.78 Calcd. for  $\text{C}_{12}\text{H}_{20}\text{O}_2$  : C, 71.38, H, 12.96%.

### III Studies on Dodecanal

In 1880 dodecanal, melting at 44.5 $^\circ$ , was prepared by Krafft<sup>6)</sup> through drydistillation of a mixture of barium-laurate and-formate. Since then Zaar<sup>7)</sup> Prepared dodecanal by the same method and purified it through sodium bisulfite addition compound. However dodecanal thus obtained melted at 11.1 $^\circ$ . On conservation of the latter a crystalline compound of mp. 44.5 $^\circ$  was deposited, which was determined as a monomer by

5) Ueno, J. Chem. ind. Japan, 52 142 (1949) (in Japanese)

6) F. Krafft, Ber. 13 1413 (1880)

7) B. Zaar, J. Prakt. Chem. 132 169 (1931)

cryoscopic observation and converted to dodecanal of mp. 11.1° by distillation under diminished pressure. Zaar suggested these two dodecanals having different melting points would be in keto-enol tautomerism and the dodecanal melting at 44.5° would be the enol-form. Furthermore he reported that a molecular compound of dodecanal and dodecanol, melting at 44.5° was obtained,<sup>8)</sup> and although dodecanal and the molecular compound melted at the same temperature the two compounds were quite different. <sup>7)</sup>

Lately Komori<sup>9)</sup> suggested that Krafft's dodecanal would be the molecular compound whereas Zaar's dodecanal, melting at 44.5° would be dodecanal impurified by lauric acid which produced by autoxidation of dodecanal.

It has now been shown that Krafft's aldehyde of mp 44.5° is a molecular compound.

On dry distillation of a mixture of barium-laurate and bariumformate dodecanal of mp. 11.8° was obtained as the chief product and as a by-product a solid melting at 44.5° from which dodecanol was isolated.

On conservation in a sealed tube dodecanal of mp. 11.8° polymerizes to its trimer melting at 56~56.5°, named as paradodecanal, and exists as an equilibrium mixture with paradodecanal. Zaar's dodecanal, considered by him to be the enol form, melting at 44.5° was not found,

Paradodecanal depolymerized to dodecanal in a good yield when distilled under diminished pressure.

The polymerization of dodecanal to paradodecanal was catalyzed with sulfuric acid, hydrochloric acid, etc. as in the lower homologues.<sup>10)</sup>

## Experimental

### Synthesis of dodecanal

A mixture of barium-laurate (30g), barium-formate (30g) and barium carbonate (5g) was dry distilled under diminished pressure (4~12mm), yielding 15g of the distillate.

The distillate (50g) was subjected to three successive fractional distillations in a stream of hydrogen under diminished pressure.

(I) at 2mm.		mp*
Distillate (1)	85~96°	6.8g
" (2)	96~99°	18.6g 43.5~44.5°
" (3)	99~104°	10.1g 42~45°
Distillate (4)	residue	12.8g

(II) The distillate (2) was rectified at 2 mm

Distillate 1	88~96°	1.2g
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8) B. Zaar, J. Prak. Chem. 132 163 (1931)

9) Komori, J. hem. ind. Japan 53 44 (1950) (in Japanese)

10) Wakayama, J. Chem. Soc. Japan 72 275 (1951) (in Japanese) C. A. 46 2483 (1952)

\* m. p. of the substance dried on porous sheet.

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2	96~98°	15.3g	
3	98~100°	1.4g	mp 42~44.5°

Distillate (3) and 3 melted at 43.5~44.5° after recrystallization from ether.

The crystals melting at 43.5~44.5°, when treated with phenyl isocyanate, gave a dodecyl phenylurethane melting at 74~74.5° after recrystallization from ethanol  
Found : N 4.52, Calcd. for  $C_{19}H_{31}O_2$  : N, 4.59%

(III) The distillate 2 was rectified at 2.5mm.

mp			
Distillate (1)	94~96°	0.5g	
(2)	96~98°	12.8g	11.8°
(3)	98~100°	0.6g	42~44
(4) residue	0.8g		53.5~54°

The m. p. and bp. of the distillate (2) coincided well with those previously reported by Zaar<sup>7)</sup>. Oxim prepared by the usual way melted at 77.5~78° after recrystallization from ethanol, identified as dodecanal oxim.

The residue (4) by recrystallization from ethanol yielded colorless needles melting at 55.5~56°, identified as paradodecanal by comparison with an authentic specimen.

### Spontaneous polymerization

Dodecanal (b<sub>2</sub> 96~97°, m. p. 11.8°) when preserved in a sealed tube separated no precipitate in four months.\*

The preserved dodecanal was rectified at 2.5mm.

Distillate (1)	94~96°	0.3g
" (2)	96~98°	3.8g
" (3)	98~100°	0.3g
" (4) residue		0.6g

The residue (m. p. 50~52.5°) melted at 55.5~56° after recrystallization from acetone-alcohol (1:2), identified as paradodecanal by comparison with an authentic specimen. 11)

### Catalytic polymerization

Dodecanal polymerizes exothermic to paradodecanal in the presence of a small amount of sulfuric acid, sulfurous acid,\* hydrochloric acid, ferric chloride and stannous chloride.

For instance, on addition of a trace of sulfuric acid, dodecanal (3g) was instantly solidified (under water cooling). After one hour it was dissolved in ether. The ethereal

\* Sometimes it solidified, but from the solid which melted at 55.5~56° after recrystallization from acetone-alcohol, dodecanal was obtained in ca 80% yield by distillation under diminished pressure. That such a difference occurred in the preservation of dodecanal would depend on the different velocity of polymerization owing to the different amount of lauric acid (the concentration of proton) produced by autoxidation.



solution was washed with water, dried with anhydrous sodiumsulfate, and the ether removed, yielding a solid melting at 54.5~56° (2.8g). After recrystallization from acetone-alcohol (1:2) it melted at 56~56.5°, and was easily soluble in benzene and chloroform, soluble in ether, acetone, and sparingly soluble in alcohol. Negative to Schiff's aldehyde reagent and silver mirror-test of ammoniacal silver nitrate. Found : C, 78.75, H, 12.93 : Mol. wt.(cryoscopic, benzene)518.5, 525, Calcd. for  $(C_{12}H_{24}O)_3$  : C, 78.28, H, 13.33% : Mol. wt 552.

#### Depolymerization of paradodecanal

Depolymerization of paradodecanal to dodecanal is accomplished by distillation under diminished pressure with a trace of a polymerization catalyst such as sulfuric acid. The depolymerization is also accomplished merely by distillation under diminished pressure without catalyst.

For instance, paradodecanal (2g) when subjected to distillation at 2.5mm., was distilled at 70~180° (yield 1.7g). The distillate was returned into the flask and redistilled at 1.5mm., when dodecanal was distilled out at 92~93° (yield 1.6g).

The second distillation proceeded smoothly.

Oxim easily prepared in the usual way melted at 78~78.5° after recrystallization from ethanol.

### IV Syntheses of Higher Aliphatic\*\*

#### $\alpha\beta$ -Unsaturated Aldehydes—(I)

A number of higher aliphatic  $\alpha\beta$ -unsaturated aldehydes have been isolated as the fragrant constituents of plants, and one of the homologs has been found to have an antifungal effect.

Hexen-2-al-1 was found to be the fragrant constituent of green tea<sup>12)</sup> and it has been isolated by Onoue<sup>13)</sup> from whale oil.

Decen-2-al-1 was found in the essential oil derived from the leaves, petioles and rhizomes of coriandrum sativum during the flowering state<sup>15)</sup>, and from sweet orange<sup>16)</sup>.

Dodecen-2-al-1 was obtained by Koolhaas<sup>17)</sup> as the main constituent of volatile oil derived from the leaves of Eryngium foetidum L., Kosuge<sup>18)</sup> also found it as an antifungal principle in the essential oil derived from Houttuynia cordata Thumb

\* By Zaal<sup>17)</sup> dodecanal polymerized to a dimer, when treated with sulfurous acid. By the author the polymer was determined as a trimer by cryoscopic observation. Found : Mol wt. 578 Calcd. for  $(C_{12}H_{24}O)_3$  : 552.

11) Le Sueur, Soc: 85 382, 87 1896, 1900, 1903.

\*\* Already published in Japanese J. Chem. Soc. Japan 78 1525 (1957)

12) Takei, Bulletin Sci. Res. Inst. 12 13 (1933) (in Japanese)

13) Onoue, J. hem. Soc., Japan 73 275 (1952) (in Japanese)

14) P. van Romburgh, Rec. trav.chimi. 57 495 (1938)

15) Carlbrom, J. Prak. Chem. 144 225 (1936)

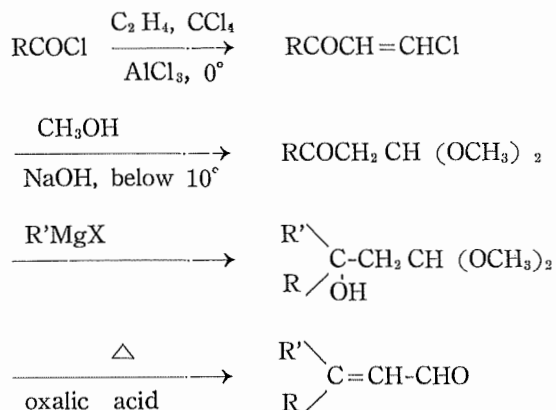
16) Naves, Perfumery Essent. oil Recd. 38 295 (1947)

("Dokukami" in Japanese).

Though several methods for obtaining aliphatic  $\alpha\beta$ -unsaturated aldehydes having a straight carbon chain are known, the most available and only method is that of v. Braun.<sup>19)</sup>

In 1950 aliphatic  $\beta$ -methyl- $\alpha\beta$ -unsaturated aldehydes having four to nine carbon atoms were synthesized by Price et al.,<sup>20)</sup> starting from acid chloride via four steps.

The reaction sequence is shown as follows :



In this method the stages of reduction and dehydration have now been properly modified, applying Meerwein-Ponndorf's method and dehydration, which was accomplished by heating in the presence of a small quantity of iodine in toluene.

A new useful method of synthesis of normal aliphatic  $\alpha\beta$ -unsaturated aldehyde has now been established.

Octadecen-2-al and decen-2-al have thus synthesised in a good yield.

The  $\alpha\beta$ -unsaturation of the aldehyde was confirmed through oxidation of octadecenal with potassium permanganate and silver oxide, yielding palmitic acid and octadecenoic acid respectively.

On hydrogenation of octadecenal and decenal in the presence of platinum oxide each two moles of hydrogen were absorbed and octadecanol and decanol were obtained.

Ultraviolet absorption maximum of decenal semicarbazone coincided well with that of crotonaldehyde semicarbazone. ( $\lambda_{\text{max}}$  262 m $\mu$ )

It is noteworthy, furthermore,  $\beta$ -hydroxy aldehyde polymerizes to a dimer immediately after its formation, similar to a ring formation of acetaldol as a dimer.\*

17) Koolbaas, Rec. trav. chim. 51 460 (1932)

18) Kosuge, J. Pharm. Soc. Japan 72 1227 (1952)

19) von Braun, Ber. 67 269, 1735 (1934)

20) Charles C. Price, J. Am. chem. Soc. 72 2613 (1950)

\* R. H. Saunder, J. Am. Chem. Soc. 65 1309 (1943) :

E. Späth, Ber 75B, 1029 (1942) : Chem Abst 37 4695 (1943)

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## Experimental

### $\beta$ -Chlorovinyl ketone<sup>21)</sup>

In a four neck-flask, pulverized aluminum chloride (1.1 Mol.) was suspended in ca 300cc of carbon-tetrachloride, and into the stirred mixture carbon tetrachloride solution of acid chloride (1 Mol 2: 1) was added dropwise over a period of 20 minutes. Acetylene was bubbled through the stirred suspension\* maintained at 0°~5° for 3 hours at a rate escaping the excess of acetylene constantly.

The reaction mixture was decomposed with ice-water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate and the ether was removed, producing crude  $\beta$ -chlorovinyl ketone in 70~80% yield.

$\beta$ -chlorovinyl heptyl ketone was obtained in a 68% yield by distillation of crude substance under diminished pressure,  $b_{3.6}$ , 62~63°.

$\beta$ -chlorovinyl pentadecyl ketone was prepared by the same method as in the above. It melted at 60.5~61° after recrystallization from ethanol (y. 72%).

Ultraviolet absorption maximum of  $\beta$ -chlorovinyl heptyl ketone (1/170 mol/1) was at 229m $\mu$ , that of  $\beta$ -chlorovinyl-pentadecyl ketone (1/1300 mol/1) at 228~230m $\mu$ .

### $\beta$ -ketoaldehyde dimethyl acetal

The general procedure of Panizzi<sup>22)</sup> and Price<sup>20)</sup> was followed. A solution of sodium hydroxide (7.1g) in 70cc of absolute methanol was added dropwise to a stirred solution of  $\beta$ -chlorovinylheptyl ketone (25g) in 100cc of absolute methanol at 10~15° over a period of 20 minutes. After being allowed to stand over night the reaction mixture was poured onto water and extracted with ether. The ether extract was washed with water, dried and the ether removed. The residue (26.5g), on fractionation, gave a colorless oil (22.5g) distilling at 110~112° at 4.5mm.  $d_4^{20}$  0.9254,  $n_D^{20}$  1.4372, MR. : Lorentz-lorenz. 61.26 ; Eisenrohr, 60.91 (keto-form), 61.96 (enol-form). Semicarbazone synthesized in the usual way melted at 81.5~82°. Found : N, 15.62, Calcd. for C<sub>13</sub>H<sub>27</sub>O<sub>3</sub>N<sub>3</sub> : N, 15.37%.

$\beta$ -keto octadecenenal dimethyl acetal was prepared from  $\beta$ -chlorovinyl pentadecylketone by the same method as above described for  $\beta$ -ketodecanaldimethylacetal. It melted at 25.2~25.7° after recrystallization from dilute ethanol (y. 87%). Semicarbazone melted at 85~86°. Found : N, 10.24, Calcd. for C<sub>21</sub>H<sub>43</sub>O<sub>3</sub>N<sub>3</sub> : N. 10.89%.

$\beta$ -ketodecanal dimethylacetel as well as  $\beta$ -ketoctadecanal dimethyl acetal gave a deep red color with alcoholic ferric chloride.

\* Aluminum chloride was dissolved and homogeneous solution was obtained in about 30 minutes.

21) Wakayama, J. Chem. Soc. Japan 76 9 (1955) (in Japanese) Org. Synth. 32 27 (1952)

22) Luigi Panizzi, C. A. 42 5877 (1948)

$\beta$ -Hydroxyaldehyde dimethylacetal

A molar isopropyl alcohol solution of 38g of aluminium isopropoxide (6.6 equivalent to ketone) was poured into a Claisen flask containing 18.5g of  $\beta$ -ketodecanal dimethylacetal and distilled slowly on a boiling water bath.\* After about 5 hours acetone could not be detected in the distillate (dinitrophenylhydroazone)<sup>23)</sup>

The residue was decomposed with 2N-potassium hydroxide and ice, extracted with ether, washed with water, dried over anhydrous sodium sulfate and the ether removed. The residue (19g) distilled at 114~115° at 4mm; yield 13.9g;  $d_4^{21.5}$  0.9206,  $n_D^{21.5}$  1.4403, MR: Lorentz-lorenz. 62.54, Eisenrohr 62.43.

$\beta$ -hydroxy octadecanal dimethyl acetal was prepared by the same way as above described. The reaction product could scarcely distill without decomposition at 2~3mm, so it was difficult to purify by distillation. Yield 85% (crude substance). mp. 27~28.5°, easily soluble in methanol, acetone, petroleum ether, chloroform and ether. Crude substance itself was used for the next reaction.

 $\beta$ -Hydroxyaldehyde

The solution of  $\beta$ -hydroxydecanal dimethyl acetal (1g) and 2 N-hydrochloric acid (0.5cc) in acetone was allowed to stand for 3 hours at a room temperature.

The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with water, dried and the ether removed.  $\beta$ -Hydroxy decanal to the amount of 0.95g was obtained, of which purification by distillation at 2~3mm was impossible owing to its easy decomposition on heating. The molecular weight of raw substance was determined by cryoscopic observation: Mol wt. 375. Calcd. for  $C_{20}H_{40}O_4$  344. It has polymerized to a dimer.

The color reaction with fuchsin sulfurous acid solution was slow but intensive. Semicarbazone prepared in the usual way melted at 125~126° and was easily soluble in methanol and ethyl acetate, insoluble in petroleum ether and benzene. Found: N, 17.86, Calcd. for  $C_{10}H_{23}O_2N_3$ : N, 18.32%.

$\beta$ -Hydroxyoctadecanal was prepared by allowing the solution of  $\beta$ -hydroxyoctadecanal dimethylacetal in 2 N-hydrochloric acid (1cc) and acetone (19cc) to stand for 3 hours at a room temperature.\*  $\beta$ -Hydroxyoctadecanal thus precipitated was collected on a suction filter. The yield was 0.85g. It melted at 94~95° after recrystallization from acetone. Mol. wt. (Cryoscopic, benzene): 610 Calcd. for  $C_{36}H_{72}O_4$ : 568. Found: C, 76.12, H, 12.44, Calcd. for  $C_{36}H_{72}O_4$ : C, 76.06, H, 12.68 Soluble in ethanol and acetone, sparingly soluble in benzene. Semicarbazone melted at 121.5~122.5°.

Found: N, 12.40 Calcd. for  $C_{19}H_{39}O_2N_3$ : N, 12.30%

\* Distilled at a rate of 1 drop per 2~3 seconds, supplying isopropylalcohol corresponding to the amount of distillate constantly.

23) R. Adams, Org. react. Vol. 2 p. 178 (1944)

Q. P. Cole, J. Chem. ed. 28 142 (1951)

\* In about fifteen minutes  $\beta$ -hydroxyoctadecanal began to crystallize.

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### $\alpha\beta$ -Unsaturated Aldehyde

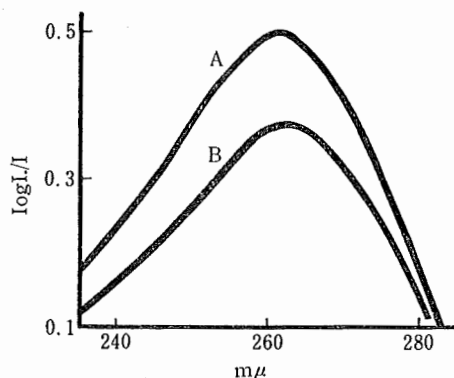
#### Decenal

The solution of  $\beta$ -hydroxydecanal (1 g) in toluene (15cc) with a trace of iodine was heated under reflux for 1 hour. On cooling, the reaction mixture was dissolved in ether. The ether solution was washed with sodium thiosulfate solution (N) and then with water, dried and the ether removed. After toluene was removed under diminished pressure, the residue subjected to distillation at 3mm. Decen-2-al-1 was obtained to the amount of 0.85g distilling at 78~80°. Positive for the tests both of ammoniacal silver nitrate and of fuchsin sulfurous acid solution.  $d_4^{20}$  0.8489,  $n_D^{20}$  1.4527 Mol. wt. (Cryoscopic, benzene) 145Calcd. for  $C_{10}H_{18}O$  : 154.

By catalytic hydrogenation with platinum oxide two moles of hydrogen were absorbed, yielding decanol ( $b_{13}$  108~109°, phenylurethane melted at 61~61.5°<sup>24)</sup>).

Semicarbazone melted at 162°.<sup>25)</sup> Found : N, 19.52, Calcd. for  $C_{11}H_{21}ON_3$  : N, 19.88%.

The ultraviolet absorption maximum of decenal semicarbazone (at 262m $\mu$ ) was similar to that of croton aldehyde semicarbazone (at 262~263m $\mu$ ) as indicated in the following figure.



In the figure decenal semicarbazone is indicated by curve (A), Croton aldehydesemicarbazone, curve (B). solvent : methanol. Concentration : ca 1/60000 mol/l.

The odor of decen-2-al-1 is chiefly composed of that of general higher aliphatic aldehyde which reminds one of *Houttuynia cordata* Thumb (Dokudami), accompanying to a certain extent by a refreshing scent. In a dilute solution it would give a violet-like fragrance for a compounding perfume, and as food adjunct would give a refreshing flavor to orange oil.\*

24) H. Meyer, *Nachw. u. Bestim. org. verbdgen.* S. 36 (1933)

25) cf. Reference 14

\* The author indebted to Dr. S. Katsura, chief engineer of the Takasago Perfumery Co. for interpretation of the odor.

Octadecenal

Octadecenal was prepared from  $\beta$ -hydroxyoctadecanal in the same way as above described for decenal. (yield 68%).  $b_{2.5}$  158~160° Found : C, 81.09, H, 12.80, Calcd. for  $C_{18}H_{34}O$  : C, 81.12, H, 12.86%. positive for the silver mirror test of ammoniacal silver nitrate and Schiff's aldehyde reagent (Slow, but intensive).

It quickly decolorized potassium permanganate solution at a room temperature. Absorption of bromine in chloroform solution was very slow. Gave no color reaction with tetranitromethane.

By catalytic hydrogenation with platinum oxide two moles of hydrogen were absorbed, producing octadecanol (mp 58~60°, octadecanol phenyl urethane melted at 76~77°, Found : N, 3.31. Calc. for  $C_{26}H_{44}O_2N$  : N, 3.60%).

Octadecenal semicarbazone melted at 153~154°. Found : N, 12.76 Calcd. for  $C_{19}H_{37}ON_3$  : N, 13.00%.

Odor of octadecenal is that of higher aliphatic aldehydes which resembles that of *Houttuynia cordata* Thumb (Dokudami), accompanying by a paraffinic scent, but very faint.

Oxidation of octadecenal with Potassium permanganate.

A 4% potassium permanganate solution was added dropwise to a stirred suspension of octadecenal (0.5g) in 10cc of 2N potassium carbonate until the violet color of permanganate no longer disappeared. The reaction mixture was allowed to stand on the boiling water bath for 30 minutes and was filtered off from the manganese dioxide. The filtrate was acidified with sulfuric acid and extracted with ether. The ether extract was washed with water, dried, and the ether removed. The residue after recrystallization from ethanol melted at 59.5~60°. NV 211 (calcd. for  $C_{16}H_{32}O_2$  : 218.9) Anilide prepared by boiling with aniline melted at 87° Found : N, 4.02%. Calcd. for  $C_{22}H_{37}ON$  : N, 4.23%.

The acid thus obtained by oxidation was palmitic acid.

Oxidation of octadecenal with silver oxide.

Alcoholic potash ( $1/2N$ ) was added drop by drop to an alcoholic solution of octadecenal (0.3g) in which 0.4g of silver nitrate was dissolved. After the reaction mixture was allowed to stand for 24. hours in darkness with shaking, it was filtered off from silver. The filtrate was diluted by three times its volume of water, and extracted with ether. The alkaline solution was acidified with sulfuric acid and extracted with ether. From the ether extract it was converted again to potassium salt with N-potassium hydroxide. The alkaline solution was acidified with sulfuric acid, extracted with ether, washed with water, dried and the ether removed. The residue melted at 56.5~57°

after recrystallization from petroleum ether and ethanol.

This melting point coincides with that of trans-2-octadecenoic acid (58.5°<sup>26)</sup> NV 190 (Calcd. for C<sub>18</sub>H<sub>34</sub>O<sub>2</sub> : 198).

## V Syntheses of Higher Aliphatic

### $\alpha,\beta$ -Unsaturated Aldehydes—(II)

In the previous chapter a new method of preparation of normal aliphatic  $\alpha,\beta$ -unsaturated aldehydes was described.

The method has next been extended to the preparations of homologs with satisfactory results.

## Experimental

### $\beta$ -Chlorovinyl ketone

$\beta$ -Chlorovinyl ketones (RCOCH=CHCl) were prepared by the same method as previously described (Chapter IV).

Their name (R), boiling point (° /mm), mp (° ), Analysis (Cl %) and yields ( %) are as follows :

R	b. p	m. p	Analysis		Yields
			Found.	Calcd.	
Hexyl-*	86 ~ 87/5.5	—	20.11	20.29	80
Octyl-**	111 ~113/5	20~21	17.35	17.49	77
Npnyl-	125 ~127/4	35~35.5	16.02	16.35	58
Decyl-	132 ~134/4	32~32.5			54
Dodecyl-		41~42			77
Tridecyl-		53.5~54.5	12.91	12.99	64
* d <sub>4</sub> <sup>21</sup> 0.9871, n <sub>D</sub> <sup>21</sup> 1.4646					
** d <sub>4</sub> <sup>21</sup> 0.9695, n <sub>D</sub> <sup>21</sup> 1.4652					

### $\beta$ -Ketoaldehyde dimethylacetal

$\beta$ -Ketoaldehyde dimethyl acetals (RCOCH<sub>2</sub>-CH (OCH<sub>3</sub>)<sub>2</sub>) were prepared in the same way as described. in the previous chapter

Their name, boiling point (° /mm), specific gravity (d<sub>4</sub><sup>21</sup>), refractive index (n<sub>D</sub><sup>21</sup>) and yields ( %) are as follows :

Name	bp	d <sub>4</sub> <sup>21</sup>	n <sub>D</sub> <sup>21</sup>	Yields
Ketnonanal dimethyl acetal	97~99°/4	0.9295	1.4260	64
Ketoundecanal dimethyl acetal	119~121°/4	0.9290	1.4385	79.4

26) G. S. Meyers, I. Am. Chem. Soc. 73 2100 (1951)

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Ketododecanal dimethyl acetal	128~129°/3.5	0.9120	1.4388	71
Ketotridecanal dimethyl acetal	141~143.5°/4	0.9118	1.4392	74
Ketohexadecanal dimethyl acetal	157~159°/3	0.8990	1.4532	54.3
Ketohexadecanal dimethyl acetal	177~179°/4	0.8996	1.4500	60

$\beta$ -Hydroxy aldehyde dimethylacetal

$\beta$ -Hydroxyaldehydedimethylacetals ( $\text{RCH}(\text{OH})\text{CH}_2\text{CH}(\text{OCH}_3)_2$ ) were prepared by the same method as previously described. Their name, boiling point ( $^\circ/\text{mm}$ ), specific gravity ( $d_4^{20}$ ), refractive index ( $n_D^{20}$ ), molecular refraction (MR) and yields (%) are as follows :

name	b. p.	$d_4^{20}$	$n_D^{20}$
Hydroxynonanal dimethyl acetal	109~110°/4	0.9315	1.4383
Hydroxy undecanal dimethyl acetal	131~133/4	0.9227	1.4456

M. R

Rorentz-	Eisenrohr	Yields*
57.62	57.60	56
67.09	67.03	66

\* substance purified by distillation,

Dimethyl acetals of  $\beta$ -hydroxy dodecanal,  $\beta$ -hydroxy tridecanal,  $\beta$ -hydroxypentadecanal and  $\beta$ -hydroxy hexadecanal were scarcely distilled without decomposition under reduced pressure (2~3mm), so crude substances themselves were used for dehydration. Their properties were not observed

$\alpha\beta$ -Unsaturated aldehyde

$\alpha\beta$ -Unsaturated aldehydes ( $\text{RCH}=\text{CH}.\text{CHO}$ ). were prepared in the same way as previously described. Their names/, boiling point ( $^\circ/\text{mm}$ ), specific gravity ( $d_4^{20}$ ), refractive index ( $n_D^{20}$ ), melting point of semicarbazone and yield (%) are as follows :

name	bp	$d_4^{20}$	$n_D^{20}$	mp. semicarb.	Yield
nonenal	58~60/3	0.8523	1.4520	164.5~165	82
undecenal	93~95/3	0.8535	1.4568	161~161.5	74
tridecenal	115~116/3	0.8534	1.4600	160 ~161	75
hexadecenal*	130~135/3	—		158 ~159	65

\* Hexadecenal was obtained as a liquid by distillation, but on conservation it precipitated over a period of 48 hours. The separated solid melted at 32~33°.

Mol. wt. (Rast) 628. Calcd. for  $\text{C}_{48}\text{H}_{90}\text{O}_3$  : 714.



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$\alpha\beta$ -unsaturated aldehydes has as its chief element the odon of higher aliphatic saturated aldehydes which recall *Houttuynia cordata* Thumb (Dokudami). Nonenal is more refreshing than decenal (cf. the odor of decenal). Tridecenal is accompanied with a paraffinic scent. Hexadecenal is almost odorless.