IX.—*Condensation-products of Cenanthaldehyde (Part II).*

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Action of Nascent Hydrogen on Cenanthaldehyde.

IN the preparation of heptyl alcohol by the action of nascent hydrogen on cenanthaldehyde, there is always a considerable quantity of a high-boiling bye-product formed, which often amounts to 20 per cent. of the cenanthaldehyde used. This remains in the retort, on distilling off the heptyl alcohol, as a thick brown oil, which, however, does not seem to have been investigated. As it was probable that these oils were simply condensation-products, produced by the dehydrating action of the agents used, and possibly acted on by the nascent hydrogen; it was thought that they might yield interesting results upon examination. The inquiry was divided into two parts: (1), action of nascent hydrogen on cenanthaldehyde in acid solution; (2), in ethereal solution.

(1.) *Action of Nascent Hydrogen on Cenanthaldehyde in Acetic Acid Solution.*

The operations were conducted in the same manner as described in Part I, in the section on the action of nascent hydrogen in acid solution on the aldehyde $C_{14}H_{26}O$. It is practically the same as that employed by C. F. Cross (*Jour. Chem. Soc.*, **32**, 123) for the preparation of heptyl alcohol. 200 grams of cenanthaldehyde were used in each operation, and about twice as much sodium amalgam as theoretically required for the formation of heptyl alcohol.

At the end of the reaction water was added, and the oil, after being washed, was boiled with a dilute solution of potash, in order to decompose acetates, which are always formed. It was then washed, dried, and distilled under reduced pressure (350 mm.), until the temperature reached 300° . The residue was not examined. The distillate was fractioned under ordinary pressure. The principal quantity, consisting of heptyl alcohol and a small quantity of unchanged cenanthaldehyde, came over below 200° ; the thermometer then rose rapidly to 240° , between which temperature and 300° a large amount of product distilled over. This last quantity was repeatedly rectified, when three fractions were obtained, boiling between 270 — 275° , 275 — 280° , and 280 — 283° , all of about the same size. The analyses of these gaseous numbers which always came between those calculated for the alde-

hyde $C_{14}H_{26}O$, and the alcohol $C_{14}H_{28}O$, so that it appeared very probable that both were present. In order to separate them the fractions between $265-285^\circ$ were heated in sealed tubes with excess of acetic anhydride at $180-200^\circ$ for four days, and then distilled. After the acetic acid and excess of anhydride had passed over, a considerable quantity of oil was obtained boiling between $270-300^\circ$. There was, however, a dark brown residue left, which would seem to show that, as was anticipated, some aldehyde, such as $C_{14}H_{26}O$, was previously present, and had been condensed by the action of the acetic anhydride.

The oil distilling between $270-300^\circ$ was then repeatedly fractionated, and at last gave a product which boiled pretty steadily between $280-285^\circ$. It was a colourless, highly refracting oil, possessing an agreeable odour. The analysis gave the following numbers:—

- I. 0.1860 gram substance gave 0.1992 gram OH_2 and 0.5170 gram CO_2 .
 II. 0.2167 gram substance gave 0.2302 gram OH_2 and 0.6030 gram CO_2 .

	Found.		Calculated $C_{16}H_{30}O_2 =$ $C_{14}H_{27}OC_2H_3O.$
	I.	II.	
C.	75.81	75.89 per cent.	75.59 per cent.
H	11.90	11.80 „	11.81 „

This was therefore the acetate derived from the alcohol $C_{14}H_{28}O$. As this substance, from its composition, should be an unsaturated body, it was dissolved in carbon disulphide, cooled down to -10° , and titrated with bromine. The colour of the bromine disappeared instantaneously without evolution of hydrobromic acid. A quantitative experiment gave the following numbers:—

- 2.2355 grams substance took up, without evolution of hydrobromic acid, 1.3477 gram bromine = 60.3 per cent.
 Calculated for $C_{16}H_{30}O_2 + Br_2 = 62.9$ per cent.

Attempts were made to isolate the bromine addition-product, but the body decomposes on distilling off the carbon disulphide, giving off hydrobromic acid.

This acetate was saponified by boiling with alcoholic potash. On distilling off the alcohol and adding water to the residue, the alcohol $C_{14}H_{28}O$ separates as an oil. This was taken up with ether, and the ethereal solution distilled. After a few fractional distillations the principal quantity came over as a colourless oil boiling at $280-283^\circ$. Analysis gave the following result:—

- 0.1494 gram substance gave 0.1777 OH_2 and 0.4340 CO_2 .

	Found.	Calculated $C_{13}H_{26}CH_2OH$.
C	79·23 per cent.	79·25 per cent.
H	13·22 „	13·21 „

There can be no doubt that this alcohol and the acetate from which it was separated are the same bodies as those described in Part I, p. 55, as the properties of the two so closely agree. The formation of this alcohol from cenanthaldehyde is probably due to the dehydrating action of the glacial acetic acid and sodium acetate, formed in the reaction, first producing the aldehyde $C_{14}H_{26}O$, a part of which is then acted on by nascent hydrogen, yielding this product. It is practically impossible to separate the aldehyde $C_{14}H_{26}O$ from the alcohol $C_{14}H_{28}O$ by fractional distillation, but the treatment with acetic anhydride forms an easy way of separating them, as shown in Part I.

The products of the action of nascent hydrogen in acid solution, as far as they have been examined, are therefore, heptyl alcohol, probably the aldehyde $C_{14}H_{26}O$, and the alcohol $C_{14}H_{28}O$.

(2.) *Action of Nascent Hydrogen on Cenanthaldehyde in Ethereal Solution.*

This operation was conducted in the same way as that described in Part I, p. 54, where the treatment of an ethereal solution of the aldehyde, $C_{14}H_{26}O$, is described. 450 grams of cenanthaldehyde dissolved in about $1\frac{1}{2}$ to 2 litres of ether, and from 200 to 210 grams of sodium, were used in each experiment, which required from four to five days for completion.

The ethereal was separated from the aqueous solution, well washed, first with dilute hydrochloric acid and then with water, and dried over calcium chloride. The examination of the aqueous solution showed that it contained an oily acid boiling between $221-225^\circ$; it gave the following numbers on analysis:—

0·2714 gram substance gave 0·2631 gram OH_2 and 0·6400 gram CO_2 .

	Found.	Calculated for $C_6H_{13}COOH$.
C	64·31 per cent.	64·61 per cent.
H	10·77 „	10·77 „

It was therefore heptioic acid.

The ethereal solution, containing the neutral oils, was next examined. After the ether had been distilled off, the oil was fractionated in a stream of carbonic anhydride.

It began to boil at 150° , between which temperature and 200° a considerable quantity distilled over, consisting of a mixture of heptyl

alcohol and unchanged cœnanthaldehyde. The thermometer then rose rapidly to 250° , a large quantity coming over between 250 — 300° . The residue was reserved for distillation *in vacuo*, and is referred to further on. The portion boiling between 250 — 300° was several times carefully fractioned in a stream of carbonic anhydride, as the oils oxidise in the air. It was found that when cooled down to 0° all the fractions from 255 — 280° deposited crystals, some becoming almost solid. In order to obtain this solid product in a pure state, the various fractions were cooled down to -20° in a mixture of ice and hydrochloric acid, and the oil then filtered off from the crystals as quickly as possible, by means of a vacuum pump. They were then quickly pressed between filter-paper at as low a temperature as possible, and further purified by crystallisation from ether, in which they are very soluble; on allowing the solution to evaporate spontaneously, large transparent crystals, with a beautiful lustre, were deposited. These were filtered off from the ethereal solution, and placed over sulphuric acid in an atmosphere of CO_2 for some time. The following analyses were made from several preparations:—

I.	0.1693	gram substance gave	0.1977	OH_2 and	0.4939	CO_2 .
II.	0.2333	" "	0.2760	" "	0.6755	" "
III.	0.2426	" "	0.2846	" "	0.7015	" "
IV.	0.1543	" "	0.1818	" "	0.4474	" "
V.	0.1565	" "	0.1872	" "	0.4543	" "
VI.	0.1985	" "	0.2355	" "	0.5741	" "
VII.	0.1308	" "	0.1561	" "	0.3795	" "
VIII.	0.1467	" "	0.1770	" "	0.4251	" "

Found.

	I.	II.	III.	IV.	V.	VI.
C	79.56	78.96	78.86	79.07	79.17	78.88
H	12.97	13.14	13.03	13.09	13.29	13.18

Found.

	VII.	VIII.	Mean.	Theory $\text{C}_{14}\text{H}_{18}\text{O}$.
C	79.13	79.01	79.09 per cent.	79.25 per cent.
H	13.26	13.40	13.19 "	13.21 "

This substance therefore has the formula $C_{11}H_{28}O$. It is a beautiful body, crystallising in plates which melt at 29.5° . It boils without the least decomposition at $266-268^{\circ}$. It is easily soluble in carbon disulphide, ether, alcohol, petroleum ether, and chloroform. The solution in carbon disulphide, if cooled down to -10° , does not take up bromine, it therefore appears to be a saturated body. It combines very slowly with hydrogen sodium sulphite, so that, after standing for six months with a concentrated solution of the latter body, it had not quite ceased depositing crystals. The amount of the compound obtained was unfortunately too small for analysis. This body also reduces an ammoniacal silver solution, and oxidises, when left in contact with the air, but only very slowly when in the solid state. From these properties it appears to be an aldehyde. Heated with acetic anhydride for four days in a sealed tube at 180° , it did not form an acetate. Acetic anhydride appears to act on it very slowly, as on fractioning the product there was only a very small residue left in the retort above 280° . The specific gravity of this aldehyde in the fused state is—

$$\text{at } 30^{\circ} = 0.8274$$

$$\text{at } 35^{\circ} = 0.8258$$

compared with water at the same temperatures. Its formation from cenanthaldehyde may be expressed by the following equation :—

The residue left in the retort above 310° , after distilling off the aldehyde just described, was very thick and black, and was therefore first distilled *in vacuo*, and then fractioned under a pressure of 300 mm. By the first distillation a considerable quantity of an almost colourless oil distilled over between $310-350^{\circ}$. On repeatedly fractioning under the same pressure, two principal products were obtained, boiling between $315-320^{\circ}$ and $320-325^{\circ}$, of which the first was the larger. Analyses of these gave the following results :—

- I. ($320-325^{\circ}$) 0.2466 gram substance gave 0.2882 OH_2 and 0.7347 CO_2 .
- II. ($315-320^{\circ}$) 0.1782 gram substance gave 0.2084 OH_2 and 0.5332 CO_2 .
- III. ($315-320^{\circ}$) 0.1480 gram substance gave 0.1734 OH_2 and 0.4432 CO_2 .
- IV. ($315-320^{\circ}$) 0.2159 gram substance gave 0.2540 CO_2 and 0.6466 CO_2 .

	Found.					Theory $C_{21}H_{40}O$.
	I.	II.	III.	IV.		
C	81.26	81.60	81.67	81.66	per cent.	81.82 per cent.
H	12.99	12.99	13.02	13.07	„	12.99 „

This body has therefore the formula $C_{21}H_{40}O$. It is a slightly yellow, very thick oil, which does not solidify at -10° . It reduces ammoniacal silver solution, but does not appear to combine with hydrogen sodium sulphite. Heated with potash it becomes thick and black, a small quantity of a potash salt being formed. Boiling with dilute sulphuric acid also decomposes it. In order to see if it were unsaturated, it was dissolved in carbon disulphide, cooled down to -10 , and titrated with bromine. The colour of the bromine disappeared instantly. A quantitative experiment gave the following result:—

20.65 grams dissolved in carbon disulphide, took up 10.8 grams bromine without the evolution of hydrobromic acid = 52.3 per cent.

Calculated for $C_{21}H_{40}O + Br_2 = 51.9$ per cent.

It appears therefore to be an unsaturated body. Its formation from cenanthaldehyde may be represented by the following equation:—

Its specific gravity was found to be:—

at 15°	= 0.8744
at 30	= 0.8665
at 35	= 0.8637

compared with water at the same temperatures.

The yield of this body is from 5 to 10 per cent. of the cenanthaldehyde used.

The residue in the retort, boiling above 350° *in vacuo*, became solid on cooling. On extracting with ether a white solid body remained behind, which dissolved on boiling with water. On cooling, needles of calcium heptate crystallised out. A calcium estimation gave 13.44 Ca. Calculated for $(C_6H_{13}COO)_2Ca = 13.43$ per cent. Ca. The presence of this salt is probably due to the fact that the crude oil was in the first place dried over calcium chloride, which is a little soluble in the oil, and that, at the high temperature employed in the following distillations, it was converted into calcic heptate. The products of the action of nascent hydrogen in alkaline solution on cenanthaldehyde, as far as they have been examined, are therefore:—

Heptyl alcohol: heptic acid: the solid aldehyde $C_{14}H_{28}O$: and the body $C_{21}H_{40}O$.

Oxidation of the Aldehyde $C_{14}H_{28}O$.

In order to obtain some idea as to the constitution of this aldehyde, $C_{14}H_{28}O$, and of the nature of the groups contained in it, several oxidation experiments were made, much in the same way as in the case of the aldehyde $C_{14}H_{28}O$, described in Part I. The aldehyde $C_{14}H_{28}O$ was dissolved in glacial acetic acid, and one and a-half times its weight of chromic acid dissolved in glacial acetic acid slowly added, the product being well cooled after each addition. The action is very energetic, large quantities of carbonic anhydride being given off. As soon as all the chromic acid had been added, the product was heated for two hours on a water-bath to complete the oxidation. The product was treated as in the analogous experiments in Part I. The acids obtained came over between 190° and 230° , and the liquid thus obtained was separated by further distillation into two fractions boiling between $195-210^{\circ}$ and $210-230^{\circ}$. Each of these was converted into a potassium compound and then fractionally precipitated with nitrate of silver into five fractions. Silver estimations were made in each of these precipitates.

The results showed clearly that a mixture of hexoate and heptoate of silver was present. The silver salts which gave the best results were fully analysed, and gave the following numbers. Of that from the potassium salt of the acid ($195-210^{\circ}$), fractions IV and V were analysed, with the following results:—

- I. 0.2202 gram substance gave 0.1000 OH_2 , 0.2649 CO_2 , and 0.1052 Ag.
 II. 0.2479 gram substance gave 0.1121 OH_2 , 0.2939 CO_2 , and 0.1202 Ag.
 III. 0.2267 gram substance gave 0.1040 OH_2 , 0.2742 CO_2 , and 0.1083 Ag.

	Found.			Theory for $\left\{ \begin{array}{l} C_5H_{11} \\ COOAg \end{array} \right.$
	I.	II.	III.	
C	32.81	32.33	32.97 per cent.	32.28 per cent.
H	5.05	5.02	5.10 „	4.93 „
Ag ..	47.77	48.48	47.77 „	48.43 „

It was, therefore, without doubt, hexoate of silver.

Of that from the potassium salt of the acid $218-230^{\circ}$ fractions II and III were analysed with the following results:—

- I. 0.2435 gram substance gave 0.1215 OH_2 , 0.3174 CO_2 , and 0.1112 Ag.

II. 0.1533 gram substance gave 0.0759 OH_2 , 0.1975 CO_2 , and 0.0702 Ag.

III. 0.2368 gram substance gave 0.1145 OH_2 , 0.3039 CO_2 , and 0.1084 Ag.

	Found.				Theory for $\left\{ \begin{array}{l} \text{C}_6\text{H}_{13} \\ \text{COOAg} \end{array} \right.$
	I.	II.	III.		
C	35.55	35.13	35.00	per cent.	35.44 per cent.
H	5.56	5.50	5.37	„	5.48 „
Ag ..	45.66	45.79	45.77	„	45.57 „

It was, therefore, heptoate of silver. The products of the oxidation of the aldehyde $\text{C}_{14}\text{H}_{28}\text{O}$, by means of chromic acid and acetic acid, are therefore carbonic anhydride, and heptoic and hexoic acids, according to the equation—

Oxidation with silver oxide was next tried.

This experiment was made in the same way as with the aldehyde $\text{C}_{14}\text{H}_{28}\text{O}$, Part I. The acids obtained were carefully fractioned. By far the largest fraction obtained boiled between $195-230^\circ$; there was, however, a small quantity of a dark-brown residue left, which was reserved for distillation *in vacuo*. The distillate $195-230^\circ$ was converted into a potassium and then into a barium compound. This dried at $120-130^\circ$ gave on analysis the following results:—

I.	0.1666 gram substance gave 0.1013 BaSO_4 = 35.79 per cent. Ba.
II.	0.1290 „ „ 0.0785 „ = 35.78 „ „
	Calculated for heptoate of barium 34.70 per cent. „
	„ „ hexoate of barium 37.33 „ „

This barium compound was therefore a mixture of barium hexoate and heptoate, the two acids being formed as in the case of the oxidation by means of chromic acid.

The dark-brown residue remaining in the retort above 230° was first distilled under a pressure of 300° , when most of it came over at about 230° . This was then carefully fractioned at the ordinary pressure. After a small quantity of heptoic acid had passed over, the thermometer rose rapidly to 300° , almost all the product (about $1\frac{1}{2}$ grams) distilling between $300-310^\circ$. On analysis it gave the following numbers:—

I.	0.0967 gram substance gave 0.1029 OH_2 and 0.2623 CO_2 .
II.	0.1341 „ „ 0.1428 „ 0.3620 „

	Found.			Theory for $C_{14}H_{28}O_2$.
	I.	II.		
C	73.97	73.59	per cent.	73.60 per cent.
H	11.82	11.83	„	12.28 „

This acid, therefore, has the formula $C_{14}H_{28}O_2$. It is an almost colourless oil, which distils at the ordinary pressure, apparently without the least decomposition. The yield from the aldehyde $C_{14}H_{28}O$ is very small, so that it was found impossible to prepare salts pure enough for analysis.

This acid dissolves in ammonia, but the ammonium salt, on standing, quickly deposits an oil which may possibly be the amide of the acid.

The potash salt is a soap, and difficult to obtain pure. It is formed by shaking the acid with very dilute potash; on evaporating, however, it appears to decompose. The formation of this acid from the aldehyde may be expressed thus:—

By cooling to -10° it becomes very thick, but was not obtained in a solid condition.

As it seemed possible that the acid just described might be obtained in larger quantity from the aldehyde by employing an alkaline solution of potassium permanganate, the following experiment was made. About 20 grams of $C_{14}H_{28}O$ were mixed with rather more than the calculated quantity of permanganate dissolved in dilute soda, and from time to time the mixture was well shaken up. The oxidation took place rapidly at first, but afterwards proceeded very slowly. At the end of a week alcohol was added, and the soda solution separated from the precipitated hydrate of manganese by filtering through glass wool. The acids which had been formed were then liberated with hydrochloric acid, taken up with ether, and fractioned. However, almost all the acids came over between $200-230^\circ$, and only a trace of an acid with a high boiling point was present; this, however, appeared to boil at the same temperature as that obtained by the oxidation with silver oxide. The fraction boiling between $200-230^\circ$ was converted into potash salts, purified as usual with absolute alcohol, and the silver salts precipitated with nitrate of silver. Analysis gave the following result:—

0.3208 gram substance gave 0.1475 OH_2 , 0.3896 CO_2 , and 0.1567 Ag.

	Found.	Theory for $C_5H_{11}COOAg$.	Theory for $C_6H_{13}COOAg$.
C	33.12 per cent.	32.28 per cent.	35.44 per cent.
H	5.11 „	4.93 „	5.48 „
Ag ..	48.84 „	48.43 „	45.57 „

It was therefore a mixture of hexoate and heptoate of silver. The products of the oxidation of $C_{14}H_{28}O$ are therefore carbonic anhydride, heptoic and hexoic acids, and $C_{13}H_{27}COOH$.

Several attempts were made to purify the neutral oils which were obtained in these experiments by fractional distillation, but although several analyses were made of different fractions, no good results could be obtained. They begin to boil at 250° , but by far the greater part boil above 360° .

Action of Nascent Hydrogen on the Aldehyde $C_{14}H_{28}O$.

The crystalline body, $C_{14}H_{28}O$, being an aldehyde, it was thought interesting to try the action of nascent hydrogen on it, in order, if possible, to get the corresponding alcohol $C_{14}H_{30}O$. This would have the same formula as that previously obtained by the action of nascent hydrogen on the alcohol $C_{14}H_{28}O$ (Part I, p. 56). The experiment was made in the following way: The aldehyde was first dissolved in glacial acetic acid, and zinc turnings added, the whole being warmed on a water-bath. It was found advantageous to cover the surface of the zinc with copper, by dipping it in a solution of sulphate of copper, the action being thus very much accelerated. From time to time small quantities of water were added; the mixture was heated at last nearly to boiling. Water was then added in excess, and after nearly neutralising the acetic acid with potash, the oil was separated and well washed. On distilling, there still appeared to be a considerable quantity of unchanged aldehyde present, the product was, therefore, again treated with nascent hydrogen. This time, however, the oil was dissolved in ether and treated with water and sodium in exactly the same way as was employed in the reduction of cœnanthaldehyde, as it was found to give better results than zinc and acetic acid. After a considerable excess of sodium had been added, the oil was extracted from the aqueous solution with ether, then dried and fractioned. After the ether had been distilled off, the principal quantity of the product came over between 260 — 290° , only a small residue remaining behind in the retort.

This distillate was then several times carefully fractioned, the largest part obtained boiling between 270 — 275° .

On analysis it gave the following numbers:—

0.1500 gram substance gave 0.1881 OH_2 and 0.4304 CO_2 .

	Found.	Theory for $C_{14}H_{30}O$.
C	78.25 per cent.	78.50 per cent.
H	13.93 „	14.02 „

It therefore has the formula $C_{14}H_{30}O$.

It is a colourless oil, having but little odour. Cooled down to -10° it solidifies to a waxy mass, which melts again at the ordinary temperature. It does not oxidise in contact with the air. When dissolved in carbon disulphide, and cooled down to -10° , it does not take up bromine. It is soluble in most of the ordinary solvents. Its specific gravity is

at 15°	= 0.8368
at 30	= 0.8301
at 35	= 0.8279

compared with water at the same temperatures. It is, without doubt, the same alcohol as that previously obtained by the action of nascent hydrogen on the unsaturated alcohol $C_{14}H_{28}O$, as it has the same boiling point. To further establish this, however, the acetate was prepared by heating it in a sealed tube with excess of acetic anhydride at 180° for two days. On the first distillation almost all the oily product distilled over between $270-285^{\circ}$, very little residue being left in the retort.

On repeating the fractioning, the principal portion came over between $275-280^{\circ}$. On analysis it gave the following numbers:—

0.1165 gram substance gave 0.1310 OH_2 and 0.3210 CO_2 .

	Found.	Theory for $C_{14}H_{28}OC_2H_3O$.
C	75.14 per cent.	75.00 per cent.
H	12.49 ,,	12.50 ,,

The numbers agree therefore with those required for the formula $C_{14}H_{28}O.C_2H_3O$.

In order to prove that this body is an acetate, a determination of the acetic acid, formed by its saponification, was made, which gave the following numbers:—

3.5293 grams substance gave 1.3065 grams potassium acetate = 22.67 per cent. $C_2H_4O_2$. The formula $C_{14}H_{28}O.C_2H_3O$ requires 23.43 per cent.

This acetate is a beautiful colourless oil, possessing an aromatic odour. It boils at the same temperature as that described in Part I ($275-280^{\circ}$). It refracts light very strongly. Cooled to -10° it does not solidify. When warmed with alcoholic potash it is very easily decomposed into potassic acetate and the alcohol $C_{14}H_{28}O$. Its specific gravity is

at 15°	= 0.8559
at 30	= 0.8476
at 35	= 0.8448

compared with water at the same temperatures.

It is therefore seen that both the aldehyde $C_{13}H_{27}COH$, and the alcohol $C_{14}H_{27}OH$, when treated with nascent hydrogen, yield the same body, viz., the alcohol $C_{14}H_{29}OH$.

Theoretical Remarks.

As the aldehyde $C_{14}H_{28}O$ splits up on oxidation into heptoic, hexoic, and carbonic acids, according to the equation—

it must have the following constitution :—

This shows that it is a saturated body. It is isomeric with the alcohol $C_{14}H_{28}O$ described in Part I, obtained by the action of nascent hydrogen on the aldehyde $C_{14}H_{26}O$.

This aldehyde $C_{14}H_{26}O$ contains the group $\begin{array}{c} | -CH_2 \\ | \\ -CH.CO.H \end{array}$, whereas the alcohol contains the group $\begin{array}{c} | -CH \\ || \\ -C.CH_2OH \end{array}$.

The production of this aldehyde is somewhat difficult to understand, as it is not formed by the action of nascent hydrogen on the aldehyde $C_{14}H_{26}O$. It would seem to be probably formed by the action of the nascent hydrogen at the moment of the condensation of the cenanthaldehyde. A further attempt to obtain it from the aldehyde $C_{14}H_{26}O$ was made by dissolving the latter in ether, cooling in a freezing mixture, and then adding bromine. As soon as this was no longer decolorised, water was added and then sodium, till a small quantity of the ethereal solution taken out was found no longer to contain bromine. The ether was then distilled off, and the residual oil fractioned.

A considerable quantity came over between 270° — 280° , which on combustion gave numbers agreeing fairly well with the formula $C_{14}H_{30}O$; it was therefore apparently the same alcohol as that obtained by the action of nascent hydrogen on the aldehyde and alcohol $C_{14}H_{28}O$. On heating with acetic anhydride in a sealed tube, it also gave an acetate. It is quite possible that some of the aldehyde $C_{14}H_{28}O$ was formed in this experiment, but could not be separated from the alcohol $C_{14}H_{30}O$. The aldehyde $C_{14}H_{26}O$ is isomeric with myristic aldehyde, which F. Krafft (*Ber.*, **13**, 1415) obtained by the dry distil-

The constitution of the acid $C_{14}H_{28}O_2$ obtained by the oxidation of the aldehyde $C_{14}H_{28}O$, is represented thus:—

$$3\text{C}_7\text{H}_{14}\text{O} + \text{H}_2 = \text{C}_{21}\text{H}_{40}\text{O} + 2\text{H}_2\text{O},$$
$$\begin{array}{c} \text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH} \\ | \\ \text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{C}.\text{CH}_2 \\ | \\ \text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}.\text{COH}. \end{array}$$

Polymerisation of Cinnamaldehyde.

Bruylants (*Ber.*, **8**, 415) has shown that by the action of dry potassium carbonate on cœnanthaldehyde a solid polymeride of this body is produced, and it was thought that it would be of interest to make some experiments with this compound, with a view, if possible, of getting some clue as to its molecular weight, and also of comparing it with aldol. Borodin mentions that these two bodies appear to be closely related, both of them losing water on distillation, aldol giving

crotonic aldehyde; while the polymeride of cœnanthaldehyde gives the bodies $C_{14}H_{26}O$ and $C_{28}H_{54}O_3$, cœnanthaldehyde being also apparently regenerated. The latter reaction seems, however, to be more complicated than that with aldol, and the formation of the body $C_{28}H_{54}O_3$ would appear to indicate that the polymeride contained more than twice $C_7H_{14}O$. The polymeride was prepared as follows by the method used by Bruylants:—

100 grams of cœnanthaldehyde were mixed with about 20 grams of dry potassium carbonate, and allowed to stand at ordinary temperatures, the formation of the polymeride generally requiring about four days. It is, however, hastened by gently warming and shaking the mixture from time to time at about $40-45^\circ$; the polymerisation is then generally complete in 5—6 hours, the aldehyde becoming quite solid. In order to ensure the polymerisation of all the cœnanthaldehyde the mass was melted at 60° , shaken up with a small quantity of fresh potassium carbonate, and left to crystallise.

The product was carefully melted, and well washed with warm water, taking care that the temperature was not above 70° . As soon as all the carbonate was dissolved out the water was separated as much as possible, and the oil left to crystallise over sulphuric acid. This generally requires about two days. It was then placed in a vessel with a capillary tube at the bottom end connected with a vacuum pump. On working this, the oil was gradually drawn off, leaving the nearly pure polymeride as a white waxy crystalline mass. In order to free it perfectly from oil, it was pressed between filter-paper, moistened with ether, and again pressed. Obtained in this manner, it melted at $52-53^\circ$, which corresponds with the melting point found by Bruylants. The oil which was drawn off from the crystals on standing for some time at 0° , deposits a further quantity of this body in crystals—generally as long needles. By repeating this cooling process, most of the product is eventually obtained in a solid state, only a very small quantity of oil remaining. The polymeride of cœnanthaldehyde is very easily soluble in alcohol, ether, chloroform, carbon disulphide, petroleum, ether, &c., but it could not be crystallised from these solvents. It reduces an ammoniacal solution of oxide of silver very readily. If bromine be added to a solution of this body in carbon disulphide and cooled in a freezing mixture, it is not decolorised.

It was analysed, and gave the following numbers:—

0.2255 gram substance gave 0.2500 OH_2 and 0.6079 CO_2 .

	Found.	Theory for $(C_7H_{14}O)_n$.
C	73.53 per cent.	73.68 per cent.
H	12.32 „	12.28 „

As already stated, it melts at $52-53^{\circ}$, and decomposes on heating above 115° . The decomposition seems to begin at that temperature, water being given off, and collecting at the top of the vessel in which it is heated, as a cloud. In order to examine the decomposition-products of this body, 50 grams were distilled in a stream of carbonic anhydride. The substance first melts, and at about 120° froths up a little. Between 120° and 200° a good deal came over, the thermometer then rose rapidly to 270° , and between this and 300° the amount which distilled over was considerable. A small residue remained behind, which was reserved for distillation in a vacuum. It was noticed that when the substance was quickly distilled, the residue was very small, whereas if the decomposition is allowed to take place slowly, the amount of residue is increased. The oil boiling between $120-200^{\circ}$ was then several times carefully fractioned in a current of carbonic anhydride, nearly all of it at last coming over between $152-154^{\circ}$, and smelling strongly of cœnanthaldehyde. Shaken up with a solution of hydrogen sodium sulphite it combined directly, and on analysis gave the following numbers:—

0.0929 gram substance gave 0.0988 OH_2 and 0.2507 CO_2 .

	Found.	Calculated for $\text{C}_6\text{H}_{12}\text{COH}$.
C	73.59 per cent.	73.68 per cent.
H	11.81 „	12.28 „

It was therefore cœnanthaldehyde. The fraction $270-290^{\circ}$ was then several times fractioned in an atmosphere of carbonic anhydride. Almost all came over at last between $275-280^{\circ}$, and gave the following numbers on analysis:—

0.2414 gram substance gave 0.2700 OH_2 and 0.7063 CO_2 .

	Found.	Calculated for $\text{C}_{14}\text{H}_{26}\text{O}$.
C	79.79 per cent.	80.00 per cent.
H	12.43 „	12.38 „

It was therefore the aldehyde $\text{C}_{14}\text{H}_{26}\text{O}$, and was undoubtedly identical with that obtained from cœnanthaldehyde by the action of alcoholic potash, and described in Part I. Its specific gravity was practically the same, viz., 0.8504 at 15° , as compared with 0.8494. Dissolved in carbon disulphide it combines with bromine without evolution of hydrobromic acid, and does not solidify at -15° . It may be mentioned that by the decomposition of the polymeride of cœnanthaldehyde by distillation, cœnanthaldehyde and the body $\text{C}_{14}\text{H}_{26}\text{O}$ are easily obtained in a pure state, as the decomposition takes place nearly quantitatively, only a very small residue being formed. The two bodies are very easily separated by fractional distillation,

œnanthaldehyde boiling at 154° , and the aldehyde $C_{14}H_{26}O$ at 179° . The residues boiling above 290° (collected from a series of experiments) were first distilled in a vacuum, and then fractioned under a pressure of 250 mm. At the first distillation nearly all came over between 310 — 350° as a light yellow oil.

This fraction was then several times carefully fractioned under the same pressure, when most of it boiled at 330 — 340° , and gave the following numbers on analysis:—

I.	0.1211	gram substance	gave	0.1349	OH_2	and	0.3427	CO_2 .
II.	0.1324	„	„	0.1474	„	„	0.3737	„

	Found.			Theory for $C_{28}H_{54}O_3$.
	I.	II.		
C	77.18	76.98	per cent.	76.71 per cent.
H	12.37	12.37	„	12.33 „

This body seems therefore to have the composition $C_{28}H_{54}O_3$. It is an oil of a slightly yellow colour and disagreeable smell, which does not solidify when cooled down to -10° . When dissolved in carbon disulphide and cooled down to -10° , it takes up bromine without evolution of hydrobromic acid. Quantitative experiments were made with a view of determining the degree of unsaturation of the body, and gave numbers which agreed fairly well with those calculated for the formula $C_{28}H_{54}O_3Br_2$; but on titration with bromine, after a certain point is reached, the oil becomes slightly brown, and this makes it difficult to ascertain accurately when the bromine ceases to be taken up. It is apparently formed by removal of the elements of water from 4 mols. of œnanthaldehyde. Thus:—

This body reduces ammoniacal silver solution. On heating it with strong alcoholic potash it becomes brown, apparently being converted into higher condensation-products. A small quantity of potash compound was formed at the same time, which appeared to be potassium heptate. Boiling with dilute sulphuric acid also decomposes this oil.

The polymeride of œnanthaldehyde splits up, therefore, on distillation into water, œnanthaldehyde, the aldehyde $C_{14}H_{26}O$, and the body $C_{28}H_{54}O_3$. These results therefore agree with those obtained by Borodin.

In order, if possible, to get some idea as to the molecular weight of this polymeric modification of œnanthaldehyde, it was thought that by carefully distilling known quantities and then weighing the decomposition-products, *i.e.*, the œnanthol $C_{14}H_{26}O$ and the residue, some

relation might be found which would point to a probable formula. The following results were obtained from three experiments made with the pure substance :—

- I. 8.9 grams polymeride gave on distillation 4.5 grams crude cœnanthaldehyde and water, 3.7 grams $C_{14}H_{26}O$, and 0.6 gram residue (= $C_{28}H_{54}O_3$).
- II. 33.3 grams polymeride gave 16.3 grams cœnanthaldehyde and water, 14.1 grams $C_{14}H_{26}O$, and 1.3 gram residue boiling above 285° .
- III. 33.2 grams polymeride gave 16.7 grams cœnanthaldehyde and water, 14.3 grams $C_{14}H_{26}O$, and 0.9 gram residue.

The residue was all that boiled above 285° , and possibly still contained small quantities of $C_{14}H_{26}O$. These three experiments were purposely made from three different preparations. The last one was made from crystals which had separated out from the oil (obtained by filtering the crude polymeride), on standing for some weeks at 0° . The water can be calculated on the supposition that for every molecule of $C_{14}H_{26}O$ that is formed, one molecule of water is separated, which then gives the following results for cœnanthaldehyde and water :—

- I. Water calculated = 0.3 gram, therefore cœnanthaldehyde = 4.2 grams.
- II. Water calculated = 1.2 gram, therefore cœnanthaldehyde = 15.1 grams.
- III. Water calculated = 1.2 gram, therefore cœnanthaldehyde = 15.5 grams.

Calculated into percentages, the polymeride gives on distillation :—

	I.	II.	III.
Cœnanthaldehyde	47.19	45.34	46.68
$C_{14}H_{26}O$	41.58	42.34	43.07
Water	3.37	3.60	3.61
Residue	6.74	3.93	2.71

These numbers show that equal weights of cœnanthaldehyde and $C_{14}H_{26}O$ (+ water) are formed by the destructive distillation of the polymeride, *i.e.*, two molecules of cœnanthaldehyde and one of $C_{14}H_{26}O$, probably according to the equation :—

It appears therefore likely that the polymeride is formed from four molecules of cœnanthaldehyde, and has the following constitution :—

That it is a saturated body is proved by the fact, that this substance when dissolved in bisulphide of carbon, does not take up bromine without evolution of hydrobromic acid, and, if it is an aldehyde, this must also be the case from its formula. The different groups in this formula are linked together much in the same way as those in aldol, which splits up into water and crotonic aldehyde according to the equation:—

It is also very easy to understand the splitting up of the polymeride of cenanthaldehyde, in a similar way, into water, the aldehyde $\text{C}_{14}\text{H}_{26}\text{O}$, and two molecules of cenanthaldehyde; thus:—

The amount of the body $\text{C}_{28}\text{H}_{54}\text{O}_3$ formed is dependent, as before mentioned, on the rapidity of the distillation. In Experiment I, for example, the polymeride was slowly distilled, and 6·74 per cent. of residue was obtained; whereas in Experiment III the retort was heated with an open flame and the distillation conducted very rapidly when only 2·71 per cent. of residue was obtained. The amount obtained has rarely reached more than 10 per cent. The formation of this substance from the polymeride of cenanthaldehyde is in itself in

favour of this latter substance being built up from four molecules of cenanthaldehyde, as the formation of the former is then very easy of explanation; thus:—

It would be difficult to understand how such a body could be produced by the simple distillation of a mixture of cenanthaldehyde and the aldehyde $C_{14}H_{26}O$. Its constitution may probably be represented thus:—

This shows it to be an unsaturated body, which is borne out by its combining directly with bromine. By the action of solid potash at ordinary temperatures on cenanthaldehyde, Borodin states that he obtained two different polymerides; the one solid and the other liquid. In order to see if this were the case when potassium carbonate was used, the oil which was filtered off from the solid polymerides was allowed to stand at 0° till it deposited no more crystals, and then completely filtered off. Only a small quantity of oil was obtained, having the appearance of glycerol, and smelling strongly of cenanthaldehyde, whereas the solid product has very little smell. It was then left for some time over sulphuric acid. On heating, the oil began to decompose at 120° , giving off water; at a temperature of 130 — 140° the decomposition was very rapid. In order to see whether it were a different polymeride or only the solid one mixed with a little impurity which prevented its crystallising, two quantitative experiments were made and the distillation-products weighed as before. They gave the following results:—

- I. 21.6 grams of the oil gave 10.3 grams crude cenanthaldehyde and water, 8.1 grams $C_{14}H_{26}O$, and 2.4 grams residue.
- II. 12.2 grams gave 5.7 grams cenanthaldehyde and water, 4.6 grams $C_{14}H_{26}O$, and 1.0 gram residue.

If the water be calculated as before, the following amounts of cenanthaldehyde and water are obtained:—

- I. Water calculated = 0.7 gram. Cenanthaldehyde = 9.6 grams.
- II. ,, = 0.4 gram. ,, = 5.3 ,,

Calculated into percentages these give the following numbers, as the relative amounts of cenanthaldehyde and $C_{14}H_{26}O$ formed:—

Ænanthaldehyde	44·44	43·47 per cent.
Water	3·24	3·28 „
C ₁₄ H ₂₆ O	37·50	37·70 „
Residue	11·11	8·19 „

These two experiments were made from two different preparations. From these results, it appears that the oil is most probably only a mixture of the solid polymeride and a little unchanged ænanthaldehyde. By the action of potassium carbonate on ænanthaldehyde, it seems therefore that only one polymeride is formed, which is solid and melts at 52–53°. By boiling ænanthaldehyde with potassium carbonate, the same condensation-products are produced as by the distillation of the polymeride, together with potassium heptoate. It is probable that the polymeric modification of isobutaldehyde, which Urech (*Ber.*, **12**, 190; **13**, 483 and 590) obtained by the action of potassium carbonate on that aldehyde at ordinary temperatures, is derived from at least four molecules of isobutaldehyde. Urech considers that it has the constitution (C₄H₈O)₃, and describes it as a very thick oil, which can be distilled in steam. When distilled, alone, however, it decomposes into water, isobutaldehyde and condensation-products. From these he isolated a body, C₁₂H₂₂O₂ = 3C₄H₈O – OH₂.

Demtschenko (*Ber.*, **6**, 1176) also obtained a polymeride by the action of sulphuric acid on isobutaldehyde, which has the formula (C₄H₈O)₃, and which he called “paraisobutaldehyde.” It distils without decomposition, and he was thus able to determine its molecular weight by taking its vapour-density; this agreed with the formula (C₄H₈O)₃. It therefore appears that the polymeride obtained by Urech is quite a different body, possibly containing at least 4(C₄H₈O).

The same remark applies to the polymeride obtained by Borodin (*Ber.*, **6**, 982) from isovaleraldehyde, which, on distillation, splits up into water, isovaleraldehyde, C₁₀H₁₈O, and C₂₀H₃₈O₂, and the hydrate of which is produced by the action of soda solutions on this aldehyde at ordinary temperatures. This latter body has the formula (C₁₀H₂₀O₂)₂H₂O = (C₅H₁₀O)₄H₂O.

By distillation, this hydrate also splits up into water, isovaleraldehyde, C₁₀H₁₈O, and C₂₀H₃₈O₂.

Action of Nascent Hydrogen on Polymerised Ænanthaldehyde.

This experiment was made in the hope of obtaining from the polymerised ænanthaldehyde, a glycol of the formula C₂₈H₆₈O₄, by the reduction of the COH-group to CH₂OH, and of thus confirming the supposition that it is derived from 4 mols. of ænanthaldehyde.

Thirty grams of the polymeride were dissolved in ether, and then treated with 50 per cent. acetic acid, and a large excess of sodium in a flask connected with a reversed condenser. The sodium was added very slowly, and now and then a little acetic acid was poured in, to insure the contents having an acid reaction, as it appeared probable that the polymeride would be easily decomposed by caustic alkali. At the end of the reaction the ethereal solution was well washed to remove sodium acetate and acetic acid, dried, and the ether distilled off. The residual oil was then carefully fractioned. The first fraction obtained was from 100—210°, and weighed about 5 grams; the thermometer then rose rapidly to 260°, and between this and 300° about 5 grams more came over. The greater part, however, boiled above 310°, and was left behind in the retort. The product which came over between 100—210° was then repeatedly fractioned, when at last most of it came over between 174—176°, and gave the following numbers on analysis:—

0.1535 gram substance gave 0.1857 OH₂ and 0.4121 CO₂.

	Found.	Calculated C ₆ H ₁₃ CH ₂ OH.
C	73.22 per cent.	72.41 per cent.
H	13.44 „	13.79 „

It is therefore undoubtedly heptyl alcohol. On shaking it with acid sodium sulphite, a small quantity of a compound was formed, indicating that a trace of cenanthaldehyde was also present. This would account for the hydrogen being low and the carbon high in the above analysis.

The oil boiling between 250—310° was then repeatedly fractioned; a product was thus obtained boiling at 297—300°. The quantity was, however, very small, so that it was very difficult to obtain pure. It gave on analysis the following numbers:—

- I. 0.2563 gram substance gave 0.3133 OH₂ and 0.7268 CO₂.
 II. 0.1746 „ „ 0.2133 „ 0.4936 „

	Found.		
	I.	II.	Theory C ₂₁ H ₄₄ O ₂ .
C	77.34	77.10 per cent.	76.83 per cent.
H	13.58	13.57 „	13.41 „

This substance therefore appears to have the formula C₂₁H₄₄O₂. Its formation, together with that of heptyl alcohol by the action of nascent hydrogen on the polymeride of cenanthaldehyde, may be represented thus:—

This reaction can be better understood if the equation is written out as follows; thus:—

This substance is a yellowish oil, which does not solidify at -20° . If dissolved in carbon disulphide and cooled down to -10° , it does not appear to take up bromine. In order to confirm its molecular weight several attempts were made to determine its vapour-density, but as it decomposes a few degrees above its boiling point, no useful results were obtained.

I hope to have another opportunity of more thoroughly studying this interesting reaction, and more especially of examining the products boiling above 310° , which, as yet, I have not been able to obtain pure.

Action of Alcoholic Potash on Acetic Aldehyde.

A few experiments were made on the action of very dilute alcoholic potash on ordinary aldehyde, in order to see if it were possible to obtain as good a yield of crotonic aldehyde by this reaction, as of the corresponding aldehyde, $C_{14}H_{26}O$, from cœnanthaldehyde, more especially as the preparation of the former by the zinc chloride reaction is unsatisfactory, the yield being very small.

The aldehyde employed in these experiments was the so-called "concentrated solution" from Kahlbaum, which is a mixture of water, aldehyde, and a trace of alcohol. The aldehyde was mixed with a little alcohol, and then treated every day with small quantities of alcoholic potash, cooling the mixture well after each addition. After standing for some time, a considerable quantity of metaldehyde separated out in large crystals, which were filtered off. From the solution an oil was obtained, which, after washing with a solution of calcium chloride and drying, was fractionated. At first a considerable quantity of unchanged aldehyde came over, then from 90—135°

a large fraction was obtained; above 130° a dark brown residue was left, which probably contained aldol, as on further heating it decomposed, giving off water and a small quantity of an oil smelling very like crotonic aldehyde.

The product boiling between 90 — 135° was carefully fractioned in carbonic anhydride. Two fractions were obtained between 100 — 110° and 115 — 130° . The latter was by far the larger. On repeatedly fractioning the first of these, nearly all of it boiled between 102 — 106° , and gave the following numbers on analysis:—

0.2093 gram substance gave 0.1636 OH_2 and 0.5229 CO_2 .

	Found.	Calculated $\text{CH}_3\text{CH}=\text{CH}\cdot\text{COH}$.
C	68.14 per cent.	68.57 per cent.
H	8.68 „	8.57 „

It was therefore crotonic aldehyde. On standing for some few days in the air, it deposited crystals of crotonic acid, melting at 70° , whereas the pure acid melts at 72° . The second fraction, on being redistilled, eventually boiled mostly between 123 — 125° , and gave the following result on analysis:—

0.1264 gram substance gave 0.1014 OH_2 and 0.2509 CO_2 .

	Found.	Calculated $(\text{CH}_3\text{COH})_3$.
C	54.13 per cent.	54.54 per cent.
H	8.91 „	9.09 „

It was therefore paraldehyde. The yield of crotonic aldehyde was unfortunately small, but it appears probable that, by modifying the conditions, it might be improved, and this process found to be the easiest method of preparing it. Paraldehyde was the chief product of the reaction.

Finally, I append a table of the substances obtained from cenanth-aldehyde, with their boiling points and specific gravities.

Name of substance.	Boiling point.	Specific gravity compared with water at the same temperature.		
		15°	30°	35°.
Cenanthaldehyde	153—154°	0·8231	0·8128	0·8099
$C_{14}H_{26}O = \left\{ \begin{smallmatrix} C_{13}H_{25} \\ COH \end{smallmatrix} \right\} \dots$	277—279°	0·8494	0·8416	0·8392
$C_{13}H_{27}COH$	266—268°	—	0·8274	0·8258
	(m.p.—29·5°)			
$C_{13}H_{25}CH_2OH$	280—283°	0·8520	0·8444	0·8418
$C_{13}H_{27}CH_2OH$	270—275°	0·8368	0·8301	0·8279
$C_{13}H_{25}CH_2OC_2H_5O$	285—290°	0·8680	0·8597	0·8568
$C_{13}H_{27}CH_2OC_2H_5O$	275—280°	0·8559	0·8476	0·8448
$C_{13}H_{25}COOH$	275—285°	—	—	—
	(at 250 mm.)			
$C_{13}H_{27}COOH$	300—310°	—	—	—
$C_{21}H_{40}O$	310—315°	0·8744	0·8665	0·8637
	(at 300 mm.)			
$C_{28}H_{50}O$	330—340°	0·8831	0·8751	0·8723
	(at 200 mm.)			
$C_{28}H_{54}O_3$	330—340°	—	—	—
	(at 200 mm.)			
$C_{28}H_{56}O_4$	melts at 52—53°	—	—	—
$C_{21}H_{44}O_2$	297—300°	—	—	—

I cannot conclude this paper without expressing my sincere thanks to Prof. Wislicenus, in whose laboratory this research was carried out, for his kind help and advice during its progress.