PERKIN ON THE CONDENSATION-PRODUCTS OF

X.—On the Condensation-products of Isobutaldehyde obtained by Means of Alcoholic Potash.

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 $Condensation\mbox{-}products\ of\ Is obut ald e hyde.$

A SHORT time ago there appeared in the Berichte (15, 2363) an abstract of a preliminary notice by Fossek (Monatsh. f. Chem. 3, 622; C. J., Abstr., 1882, 1274), on the action of an aqueous solution of caustic potash on isobutaldehyde. As I have for some time been working on the condensation-products of isobutaldehyde produced by means of alcoholic potash, in continuation of a research on the condensation of cenanthaldehyde, on which I have been engaged for the last two years, I am compelled to publish my results, although not quite completed,

especially as they are quite different from those obtained by Fossek, alcoholic potash seeming to bring about a series of reactions differing from those obtained by the action of aqueous potash. The method employed for preparing the isobutaldehyde was the following:—100 grams isobutylalcohol and 200 grams water were put into a large flask connected with a condenser, warmed up to about 50°, and a concentrated solution of bichromate of potash, mixed with an equal volume of sulphuric acid slowly run in, the contents of the flask being well shaken after each addition, to facilitate the escape of the aldehyde as soon as formed. This concentrated bichromate solution was added, until the oily layer of isobutyl alcohol disappeared from the surface of the mixture in the flask, and the whole was then boiled to drive off any aldehyde still remaining in the liquid.

The oily part of the distillate was separated from water, dried as quickly as possible with calcium chloride, and fractioned. The portion which distilled over below 100° was collected apart, and carefully fractioned by using a tube 3 feet high, to facilitate the separation of the aldehyde from the other products. By this means the aldehyde is easily obtained pure, boiling from 60—62°. The quantity was from 50—60 per cent. of the theoretical.

The condensation with alcoholic potash was first tried in the following way:-50 grams of isobutaldehyde were dissolved in 100 grams absolute alcohol, and then a solution of 2 grams potash in 20 grams alcohol slowly added, the temperature not being allowed to rise above 30°. The mixture after cooling was then mixed with a second 2 grams potash in alcohol, and after standing for 12 hours, warmed up to 50° for about 10 minutes. It is important not to warm too long, as otherwise the condensation is apt to go too far, and only high boiling condensation-products to be produced. The liquid was left to cool, and the saline products separated from the condensed oils, by adding much water and taking the oil up with ether. If the alcohol be first distilled off, the excess of potassium hydrate and saline matter act further on the aldehyde producing higher condensation-products. aqueous saline solution from several experiments was first examined; it was thoroughly freed from oily products with ether, concentrated, and acidulated with hydrochloric acid. This caused the separation of some acids, which were extracted with ether. The ethereal solution was washed, dried over chloride of calcium, and distilled.

After the ether had distilled off, the principal part of the product came over between 145—180°. A considerable quantity afterwards passed over between 180° and 260°, leaving a thick tarry residue in the retort; the portion boiling at 145—180° consisted essentially of isobutyric acid. It was, however, purified, and converted into its silver salt. A silver determination gave the following numbers:—

0.3846 gram substance gave 0.2142 gram Ag = 55.69 per cent. Calculated for $\frac{\text{CH}_3}{\text{CH}_3}$ >CH.COOAg = 55.38 ,,

The fraction boiling between 180—260° was then several times carefully fractioned, when the largest part obtained boiled at 245—255°. This gave on analysis the following numbers:—

- I. 0·1565 gram substance gave 0·1479 gram OH_2 and 0·3839 gram CO_2 .
- II. 0.1676 gram substance gave 0.1575 gram OH_2 and 0.4111 gram CO_2 .

| Found. | | | |
|--------|-------|-----------------|----------------------------|
| | | ^ | |
| | I. | II. | Theory $C_{12}H_{22}O_3$. |
| C | 66.90 | 66.89 per cent. | 67.29 per cent. |
| н | 10.50 | 10.44 ,, | 10.28 ,, |

These numbers therefore agree with those required by the formula $C_{12}H_{22}O_3$. The body is therefore an isomeride of octylacetoacetic acid; this acid is probably formed by the action of potash on the aldehyde $C_{12}H_{22}O_2$ (which will be found described further on) according to the equation—

$$2C_{12}H_{22}O_2 + KOH = C_{12}H_{21}O_3K + C_{12}H_{24}O_2$$
.

This acid dissolves somewhat readily in dilute potash, but after standing for some time the potassium salt separates out as a gummy layer on the surface of the liquid. Attempts were also made to prepare the potassium salt by dissolving the acid in dilute alcoholic potash, passing CO_2 , and filtering off the precipitated potassium carbonate, but in this case the potassium salt was left behind, on evaporating off the alcohol, as an uninviting soap. The acid itself is a light brown oil, having but little odour; it dissolves in ammonia, and precipitates silver from a solution of silver oxide in ammonia. It distils apparently without decomposition, cooled to -10° . It does not solidify.

By the action of aqueous potash on isobutaldehyde, Fossek obtains an acid to which he assigns the formula $C_8H_{16}O_3$; this requires $\begin{cases} C = 60\cdot00 \text{ per cent.} \\ H = 10\cdot00 \text{ per cent.} \end{cases}$ It melts at 75—80°, and is therefore evidently quite different from the one described above.

The ethereal solution of the condensed oils was well washed. It was dried with chloride of calcium, and fractioned in a stream of carbonic anhydride. The fraction below 100° contained besides ether a considerable quantity of the unchanged aldehyde. That from 100—140° was very small, but between 140—180° a considerable quantity of a colourless oil was obtained, smelling strongly of camphor. The residue

in the retort was very small. The oil boiling between 140—180° was fractioned as rapidly as possible, when nearly the whole came over between 70—100°, and only a small quantity distilled over between 145—160°. There was also a considerable quantity of a high boiling product, which had been produced during the distillation, left behind.

This last fraction was once more rapidly fractioned, when the principal part distilled between 154—157°. On analysis it gave the following numbers:—

- I. 0·1156 gram substance gave 0·1170 gram $\mathrm{OH_2}$ and 0·3070 gram $\mathrm{CO_2}$.
- II. 0·1195 gram substance gave 0·1198 gram $\mathrm{OH_2}$ and 0·3168 gram $\mathrm{CO_2}$.

| | F.o. | | |
|---|-------|-----------------|---|
| | f | <u> </u> | Theory C ₁₂ H ₂₂ O ₂ . |
| C | 72.52 | 72.30 per cent. | 72.73 per cent. |
| н | 11.24 | 11.14 ,, | 11.11 ,, |

This body appears to have the formula C₁₂H₂₂O₂, and is probably formed by the separation of a molecule of water from three molecules of isobutaldehyde, thus:—

$$3C_4H_4O = C_{12}H_{22}O_2 + H_2O.$$

It is a colourless oil, having a powerful ethereal smell and burning It reduces an ammoniacal silver solution readily, and combines slowly with acid sulphite of sodium, forming an amorphous-looking mass, very slightly soluble in water, which under the microscope is seen to consist of small crystals displaying colours in polarised light. On the addition of an acid or of sodium carbonate this compound is decomposed, an oil separating out. It does not solidify when cooled If dissolved in carbon disulphide, and the solution down to -10° . cooled in a freezing mixture, it takes up bromine. It is easily decomposed by potash, apparently forming a considerable quantity of potassium isobutyrate. This oil is probably the same body as that which Urech obtained (Ber., 13, 590) by distilling the polymerised modification of isobutaldehyde produced by the action of potassium carbonate. He describes it as a colourless oil, possessing an ethereal smell, and boiling at 154°. He also notices that on distilling it decomposes, leaving a high-boiling residue in the retort.

A vapour-density which he made agreed fairly well with the formula $C_8H_{14}O$, but on analysis numbers were obtained which agreed with the formula $C_{12}H_{22}O_2$. As the substance decomposes on prolonged heating, a vapour-density has probably but little value. Fossek, by the action of sodium acetate on aqueous potash, obtained an

aldehyde $C_8H_{14}O$, boiling at $149-151^\circ$, which, however, seems to be different from the one described above, as it appears to distil without decomposition. It requires 76·19 per cent. of carbon, whereas the substance examined by me contained 72·5. By the action of $ZnCl_2$ or PCl_3 on isobutaldehyde, Fossek obtains polymerides derived from 3 mols. of isobutaldehyde.

Action of Nascent Hydrogen on the Aldehyde $C_{12}H_{22}O_2$.

This experiment was tried in order, if possible, to obtain an alcohol from the aldehyde $C_{12}H_{22}O_2$, and by this means to obtain some further clue as to its constitution. About 50 grams of the aldehyde were dissolved in 200 grams of ether, mixed with a small quantity of water, placed in a large flask connected with a reversed condenser, and sodium was added at intervals and in small pieces, the mixture being kept as cool as possible, and shaken up from time to time to dissolve out any sodic hydrate suspended in the ether. The ethereal solution was then washed, dried, and fractioned. After the ether had distilled off, most of the oil came over between 260—280°, leaving however a small residue in the retort. This oil was slowly fractioned in a Wurtz flask, with a neck about 8 inches long, when the principal portion came over between 270—275° as a colourless oil, possessing a very strong odour. On analysis it gave the following numbers:—

- I. 0.1038 gram substance gave 0.1219 gram OH_2 and 0.2721 gram CO_2 .
- II. 0·1160 gram substance gave 0·1341 gram OH_2 and 0·3029 gram CO_2 .

| | Fou | nd. | | | |
|---|-------|----------------|----|--------------------------|---------------|
| | | | | | |
| | I. | II. | | Theory C ₁₂ I | $H_{26}O_2$. |
| C | 71.49 | 71.21 per cent | i. | 71·28 per | cent. |
| н | 13.05 | 12.85 ,, | | 12.87 | ,, |

It appears therefore that an alcohol of the formula $C_{12}H_{26}O_2$, which is isomeric with ethyl propyl pinacone, had been formed, according to the equation—

$$C_{13}H_{22}O_2 + 2H_2 = C_{12}H_{26}O_2$$
.

This body does not solidify at -10° , neither does it combine with acid sodium sulphite. On distillation it appears to decompose slightly, forming lower and higher fractions. This makes it difficult to obtain it in the pure state. In order, if possible, to obtain an acetate from this body, it was treated with an excess of acetic anhydride at 180° for four hours, and then fractioned. After the anhydride and acetic acid had

been slowly distilled off, nearly all the residue boiled between 175—190°. This, on carefully refractioning, gave quantities of distillate of about the same size, boiling at 180—185° and 185—190°. Analysis of these gave the following numbers:—

- (180—185°) 0·1298 gram substance gave 0·1245 gram OH₂ and 0·3211 gram CO₂.
- II. (185—190°) 0·1336 gram substance gave 0·1311 gram OH_2 and 0·3305 gram CO_2 .

Found.

I. II.
$$C_{16}H_{30}O_4 = C_{12}H_{24}O_2(C_2H_3O)_2$$
.

C..... 67.46 67.46 per cent. 67.13 per cent.

H.... 10.66 10.90 , 10.48 ,

These numbers indicate that both specimens consisted of a diacetate of the formula C₁₆H₃₀O₄. This substance would be produced according to the equation:—

$$C_{12}H_{26}O_2\,+\, \Big(\begin{matrix} CH_3CO\\ CH_3CO \end{matrix}\!\!>\!\! O\Big)_{\!2} =\, C_{12}H_{24}O_2(C_2H_3O)_2\,+\, 2CH_3COOH.$$

A Dumas vapour-density determination was made of this body, and gave 6.289. The molecular weight should therefore be $6.289 \times 28.92 = 181.87$, whereas the theoretical molecular weight for $C_{24}H_{42}O_6 = 286$, so that apparently in this case, as with the body $C_{12}H_{22}O_2$, decomposition takes place on prolonged heating of the vapour. This acetate is a very strong-smelling body, reminding one of peppermint. These results must only be looked upon as preliminary, as owing to the very small quantity of the aldehyde $C_{12}H_{22}O_2$, at my command, it has been, up to the present, impossible to confirm them.

In order to study the higher condensation-products the isobutaldehyde was treated in the same manner as in the previous experiment, twice as much potash, however, being employed, and the temperature of the reactions allowed to rise to 45°. At the conclusion of the operation the mixture was heated on the water-bath to near its boiling point for ten minutes; it was then diluted with water, and the neutral oils were taken up with ether, separated, and treated as before. On distillation a small quantity of oil came over under 200°, which contained, besides the aldehyde $C_{12}H_{22}O_2$, a small quantity of a body boiling between 190—200°; this gave on analysis, numbers approximately agreeing with the formula $C_{16}H_{30}O_3$; the quantity was, however, too small to further examine. After this the thermometer rose rapidly to 215°, and between this and 235° about 20 grams of oil distilled over, leaving in the retort a residue which was reserved for further examination (see p. 99).

On repeatedly distilling this oil in an atmosphere of carbonic anhydride, in a long-necked Wurtz flask, eventually two principal fractions were obtained, boiling between 223—224° and 224—225°; these gave on analysis the following numbers:—

I. 0.1307 gram substance gave 0.1363 gram OH_2 and 0.3381 CO_2 . II. 0.1778 , , , 0.4576 , , , 0.4576 ,

| | For | ınd. | |
|---|-------|-----------------|-------------------------|
| | | · | Theory |
| | Ī. | II. | for $C_{20}H_{38}O_4$. |
| C | 70.55 | 70.19 per cent. | 70.17 per cent. |
| H | 11.58 | 11.45 ,, | 11.11 |

This body appears therefore to have the formula $C_{20}H_{38}O_4$. Its formation is easily understood, thus:—

$$5C_4H_8O = C_{20}H_{38}O_4 + H_2O.$$

It is an almost colourless oil, which smells strongly of camphor. When it was left in contact with hydrogen sodium sulphite for two or three weeks, with constant agitation, long transparent needles were formed; it is therefore apparently an aldehyde. It does not solidify in a freezing mixture, but becomes extremely viscid. It reduces ammoniacal silver solution, but does not quickly absorb oxygen from the air. When heated for some hours with 50 per cent. sulphuric acid, it first becomes black, giving off a considerable quantity of CO₂, and at last it becomes nearly solid. Ether removes an oil from this product which principally distils between 200—240°. There was, however, also a low-boiling body present, which I hope to investigate further.

This aldehyde, $C_{20}H_{38}O_4$, is perhaps the same body as that which Urech obtained (Ber., 13, 593) by distillation of the polymeride of isobutaldehyde produced by the action of potassium carbonate. His product was an intensely yellow oil, boiling between $230-240^{\circ}$, and gave, on analysis, C=71.50 per cent., H=11.80 per cent.; considering the wideness of the range of boiling point, these agree fairly with the numbers which I obtained. He also determined the vapour-density by Hofmann's method, and found it equal to 6.80, which gives a molecular weight = 196.70 as against 342, calculated for $C_{20}H_{38}O_4$, so that it appears that this body decomposes on the prolonged heating of its vapour. In order to confirm these results, two vapour-density determinations were made, the first by the Dumas method, the second by the Victor Meyer method.

The vapour-density obtained by the Dumas method was 6.64, which agrees fairly with the one found by Urech. The one made by the Victor Meyer method gave 5.77.

The molecular weight was therefore $28.92 \times 5.77 = 167$.

This vapour-density was taken in a lead-bath, so that the body was probably fully decomposed, as this result is about half of the calculated density. It is worth noticing that during the determination by means of the Dumas method, most of the substance distilled off when the bath was up to 240°; but it was not till the bath had gone up to 252° that all was vaporised. This seems to be a clear indication of its decomposing, as the substance used boiled between 223—224°.

By the action of aqueous potash on isobutaldehyde, Fossek obtained a body boiling at $222-223^{\circ}$, and fusing at 15.5° , to which he gave the formula $C_8H_{18}O_2$. This formula requires C=65.75 per cent., H=12.33 per cent., and a molecular weight = 146. There is no doubt it is a different body from the one described above.

Action of Acetic Anhydride on C20H38O4.

As it seemed possible that the aldehyde $C_{20}H_{38}O_4$ might, by the action of acetic anhydride, form some acetyl compound which would throw light on its constitution, the following experiments were made:—A quantity of this substance was first sealed up in a tube with a slight excess of acetic anhydride (for a monoacetate), and slowly heated till the temperature reached 180°, and then allowed to cool down. On fractioning the product as soon as the acetic anhydride and acetic acid had distilled off, nearly all came over between $235-250^{\circ}$. This was several times carefully fractioned, when at last the largest quantity was obtained boiling at $240-242^{\circ}$. On analysis it gave the following results:—

I. 0.1345 gram substance gave 0.1263 gram OH_2 and 0.3375 CO_2 . II. 0.1549 ,, , , 0.1452 ,, , , 0.3905 ,,

| Found. | | | |
|--------|-----------------|-----------------|-------------------------|
| | <i>د</i> ــــــ | | Theory |
| | `I. | II. | for $C_{22}H_{40}O_5$. |
| C | 68.43 | 68.75 per cent. | 68.75 per cent. |
| н | 10.43 | 10.42 ,, | 10.42^{-1} ,, |

These numbers agree with those required for a monoacetate, produced according to the following equation:—

$$C_{20}H_{38}O_4 + {{
m CH_3CO} \over {
m CH_3CO}} > O = C_{22}H_{40}O_6 + {
m CH_3COOH}.$$

This body is an almost colourless oil, having only a very faint smell. It does not solidify in a freezing mixture. Treated with potash it turns black, appearing to saponify very easily. In order to see if acetic anhydride had any further action on this body, it was heated in a sealed tube with excess of acetic anhydride to 200—220° for five

hours, and then refractioned. Nearly all of the oil came over between 240° and 255°. This when refractioned two or three times gave, as the principal part, an oil boiling constantly from 248—252°, and yielding on analysis the following numbers:—

I. 0·1344 gram substance gave 0·1189 OH₂ and 0·3217 CO₂. II. 0·1372 ,, ,, 0·1235 ,, 0·3389 ,,

| rouna. | | | |
|----------------------------|---------|-----------------|---------------------------|
| | ىــــــ | | Theory |
| | I. | II. | for $C_{24}H_{42}O_{6}$. |
| C | 67.31 | 67.37 per cent. | 67.60 per cent. |
| $\mathbf{H} \ldots \ldots$ | 9.83 | 10.00 ,, | 9.86 ,, |

This body may therefore be regarded as a diacetate derived from $C_{20}H_{38}O_4$, and produced from the monoacetate, according to the equation:—

$$C_{22}H_{40}O_5 + \frac{\mathrm{CH_3CO}}{\mathrm{CH_3CO}}\!\!>\!\! O = C_{24}H_{42}O_6 + \mathrm{CH_3COOH.}$$

This diacetate resembles the monoacetate in most respects; it is an almost colourless oil, has very little smell, and does not solidify in a freezing mixture. It distils without the least decomposition. In order to prove that this was really a diacetate, it was quantitatively saponified, and the acetic acid formed was determined. As there was not sufficient of the fraction 248—252°, a fraction boiling at 246—254° was taken, and gave the following results:—

4·1428 gram substance was saponified with alcoholic potash, water added, and the oil extracted with ether. The potash-solution was concentrated, acidulated with sulphuric acid, and distilled into barytawater, and afterwards the excess of baryta was separated with carbonic anhydride. The weight of barium salt obtained, after evaporation, was 3·1862 grams. As the salt did not look pure, it was thought that it probably contained a small quantity of barium isobutyrate. A barium determination was therefore made which gave 52·74 per cent.

Theory for Ba $(C_2H_3O_2)_2 = 53.72$. This therefore apparently consisted of—

Barium acetate 89.86 per cent. = 2.863 grams. Barium isobutyrate... 10.14 ,, = 0.3231 gram.

Theory requires that from 4·1428 grams of the diacetate, 2·4800 grams of barium acetate should be formed, which agrees as well as could be expected with the quantity found. There is, therefore, no doubt that it was a diacetate. The dark-brown ethereal solution, which was separated from the potassium acetate, was well washed, dried, and fractioned. After the ether was distilled off, the thermometer rose rapidly to 200°, the greater quantity coming over between 215° and

240°. A considerable quantity of a black tar was left behind in the retort, which was not further examined. The presence of this, as well as the apparent formation of isobutyric acid, shows that, besides saponifying, the potash had also exercised a further action on the product. The fraction 215—240° was then redistilled, when the principal portion passed over at 217—223°, and gave on analysis the following result:—

I. 0.1435 gram substance gave 0.1568 OH₂ and 0.3629 CO₂. II. 0.1254 ,, , , 0.1370 ,, 0.3165 ,,

| Found. | | | |
|------------------|-------|-----------------|-------------------------|
| | | Theory | |
| | Í. | 11. | for $C_{20}H_{42}O_4$. |
| C | 68.97 | 68.83 per cent. | 69.37 per cent. |
| ${\tt H} \ldots$ | 12.14 | 12.14 ,, | 12.14 ,, |

This body has therefore the formula $C_{20}H_{42}O_4$, or 4H more than the body $C_{20}H_{38}O_4$, which should have been reproduced by the saponification. This new product is an almost colourless oil, having a peculiar odour, which does not resemble that of the aldehyde $C_{20}H_{38}O_4$. The first of the above combustions is from a fraction boiling between 217—219°, and the second from a fraction (219—223°). It therefore appears that by the saponification of the diacetate, the body $C_{20}H_{38}O_4$, probably first produced, is further acted on by the reducing and oxidising action of the potash, part being oxidised and part forming the body $C_{20}H_{42}O_4$.

The residue of the condensed isobutaldehyde left in the retort and boiling above 235° was distilled under a pressure of 100 mm. A considerable quantity came over between 185° and 200°; the next large fraction was between 220—235°. The distillation was discontinued when the temperature had reached 280°, and decomposition set in. No solid bodies were obtained. The portion boiling at 185—200° was then fractioned under the ordinary pressure, when it nearly all distilled over between 245° and 260°. This was then collected between every 5°; the principal product thus obtained boiled at 250—255°.

On analysis it gave the following results:-

I. 0·1234 gram substance gave 0·1231 OH₂ and 0·3328 CO₂. II. 0·1370 ..., 0·1374 ... 0·3666 ...

| | Found. | | |
|------------------------|--------|-----------------|-------------------------|
| | | <u> </u> | Theory |
| | Ĭ. | II. | for $C_{24}H_{44}O_4$. |
| C | 73.55 | 72.97 per cent. | 72.72 per cent. |
| ${ m H} \ldots \ldots$ | 11.08 | 11.14 " | 11.11 " |
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It thus appears to have the formula C₂₄H₄₄O₄, and is probably produced according to the equation—

$$6C_4H_8O = C_{24}H_{44}O_4 + 2OH_2.$$

It is a stable body, and requires long boiling with dilute sulphuric acid to decompose it. Owing to the small quantity produced in the action of potash on isobutaldehyde, it could only be very little examined. It is an almost colourless oil, and distils at ordinary pressures without decomposition. It does not seem to combine with acid sulphite of soda. On heating with strong alcoholic potash, it turns black and is decomposed, forming a considerable quantity of a potassium salt. Two vapour-density determinations were made which gave 12.61 and 13.21.

The calculated density for $C_{24}H_{44}O_4 = 13.69$.

From these determinations, it appears evident that this body is much more stable than the lower condensation-products, as the figures obtained, although not agreeing well with the calculated ones, yet go to show that the body is produced by the condensation of six molecules of isobutaldehyde, the next lower one, $C_{20}H_{38}O_4$, having a calculated density = 11.82.

The fraction obtained between 220—235° under a pressure of 100 mm. was then carefully distilled under the same pressure. After repeating this operation several times, a considerable quantity was obtained, boiling constantly at 227—229°, which gave on analysis the following numbers:—

I. 0·1281 gram substance gave 0·1305 OH₂ and 0·3630 CO₂. II. 0·1420 ,, , 0·4038 ,,

| $\mathbf{Found.}$ | | | |
|-------------------|-------|-----------------|-------------------------|
| | | <u> </u> | Theory |
| | Ĭ. | 11. | for $C_{28}H_{48}O_3$. |
| C | 77.28 | 77.55 per cent. | 77.77 per cent. |
| H | 11.32 | 11.11 ,, | 11.11 ,, |

This body appears therefore to have the formula $C_{28}H_{48}O_3$. The formation may be expressed by assuming that four molecules of water are removed from seven molecules of isobutaldehyde according to the equation:—

$$7C_4H_8O = C_{28}H_{48}O_3 + 4OH_2$$
.

This body is a very thick yellowish oil, having a very faint smell. It distils in a vacuum without decomposition, but at ordinary pressures it appears to split up into lower and higher boiling bodies, a tarry residue being left behind in the retort. This decomposition was also seen when two vapour-density determinations were attempted. By the Victor Meyer process in a lead-bath, they gave 10.42 and 10.77.

The calculated density for C₂₈H₄₈O₃ is 14.94.

The still higher-boiling condensation-products would be very difficult to obtain pure, and were not analysed. There appeared, however, to be a definite body boiling at about 250°, under a pressure of 100 mm. A table is appended of the bodies obtained and their boiling points.

| $\begin{array}{lll} C_{12}H_{26}O_2 & & 170-175^{\circ} \\ C_{12}H_{24}O_2(C_2H_3O)_2 & & 185-190^{\circ} \\ \end{array} & \begin{cases} \text{Alcohol (and acetate)} \\ \text{produced by the action} \\ \text{of nascent hydrogen} \\ \text{on } C_{12}H_{22}O_2. \\ \end{cases} \\ C_{20}H_{37}O_4(C_2H_3O) & & 240-242^{\circ} \\ C_{20}H_{36}O_4(C_2H_3O)_2 & & 248-252^{\circ} \\ \end{cases} & \begin{cases} \text{Acetates produced by} \\ \text{the action of acetic} \\ \text{anhydride on } C_{20}H_{36}O_4. \\ \end{cases} \\ C_{20}H_{42}O_4 & & 217-223^{\circ} \\ \end{cases} & \begin{cases} \text{Produced by saponify-ing } C_{.0}H_{36}O_4(C_2H_3O)_2. \\ \end{cases} \\ C_{12}H_{22}O_3 & & 245-255^{\circ} \\ \end{cases} & \begin{cases} \text{Acid produced by the} \\ \text{action of potash on} \\ \text{isobutaldehyde.} \end{cases}$ | $egin{array}{c} C_{12}H_{22}O_2 & & & & & \\ C_{16}H_{30}O_3 & (?) & & & & \\ C_{20}H_{28}O_4 & & & & & \\ C_{24}H_{44}O_4 & & & & \\ C_{28}H_{46}O_3 & & & & \\ \hline \end{array}$ | 154—157° 190—200° 223—225° 250—255° 227—229° (100 mm. pressure) | Condensation-products. |
|---|--|--|---|
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | | | produced by the action of pascent hydrogen |
| $\{ \text{ ing } C_{.0}H_{30}O_4(C_2H_3O)_2.$ $\{ \text{Acid produced by the } \}$ | | | the action of acetic |
| | ${ m C}_{20}{ m H}_{42}{ m O}_4$ | 217—223° | $\begin{cases} \text{Produced by saponify-} \\ \text{ing } C_{.0}H_{36}\dot{O}_4(C_2H_3O)_2. \end{cases}$ |
| | $\mathrm{C}_{12}\mathrm{H}_{22}\mathrm{O}_3$ | 245—255° | |