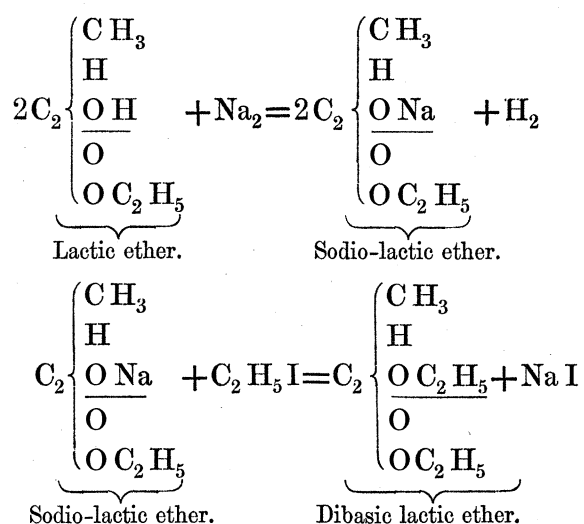


III. *Synthetical Researches on Ethers.*—No. 1. *Synthesis of Ethers from Acetic Ether.*By E. FRANKLAND, *F.R.S.*, and B. F. DUPPA, *Esq.*

Received July 13,—Read November 16, 1865.

IN his researches upon lactic acid WURTZ\* contends with considerable force for the dibasicity of this acid, supporting his view by the transformation of monobasic into dibasic lactic ether by the consecutive action of sodium and iodide of ethyl, as expressed in the following equations:



During the prosecution of our researches upon acids of the lactic series†, we have obtained several so-called dibasic ethers of this description; but before finally deciding upon the interpretation to be put upon such reactions, it appeared advisable to ascertain the effect of the same reagents upon a well-defined monobasic ether. For this purpose acetic ether was selected, and was treated, first, with sodium, and then with the iodides of ethyl, methyl, and amyl respectively. The results, although not strictly analogous with those obtained under similar circumstances with ethers of the lactic series, are highly remarkable. We have already briefly referred to them in a note presented to the Royal Society in April 1865‡.

*Action of Sodium and Ethyl Iodide upon Acetic Ether.*

The acetic ether used for this and the succeeding reactions was made as follows:—

6000 grms. of previously dried and fused sodium acetate was broken into small pieces

\* Ann. de Ch. et de Phys. t. lix. p. 161.

† Proceedings of the Royal Society, vol. xii. p. 396; vol. xiii. p. 140; vol. xiv. pp. 17, 79, 83, 191, and 197.

‡ *Ibid.* vol. xiv. p. 198.

and placed in a copper still immersed in cold water. Over this was gradually poured 12600 grms. of a mixture of 3600 grms. alcohol\* of 97 per cent., and 9000 grms. concentrated sulphuric acid, taking care that the temperature did not rise high enough to distil off any of the product. The success of the operation depends greatly upon the mode of mixing the alcohol and sulphuric acid, which ought to be performed as follows. The sulphuric acid being placed in a deep stoneware vessel of sufficient capacity, the alcohol is conducted to the bottom of it by means of a piece of narrow glass tube, connected by a caoutchouc tube with a convenient reservoir standing at a considerable elevation. The glass tube is used as an agitator during the continuance of the flow of the alcohol. In this way there is obtained, without loss of alcohol, a high temperature which greatly favours the formation of sulphovinic acid. This mixture must be allowed to stand, carefully covered up, for twenty-four hours before use.

It is also advisable to make the admixture of sulphovinic acid and sodium acetate at least twelve hours before the distillation is commenced. The latter operation can then be performed over a naked fire or gas-flame, and continued till water alone passes over. In this way there was obtained 6000 grms. of an acetic ether absolutely free from alcohol, and which, without previous washing, only needs one rectification from fused and powdered chloride of calcium to fit it for the action of sodium. A determination of its vapour-density gave the number 2.9. Pure acetic ether requires 3.04.

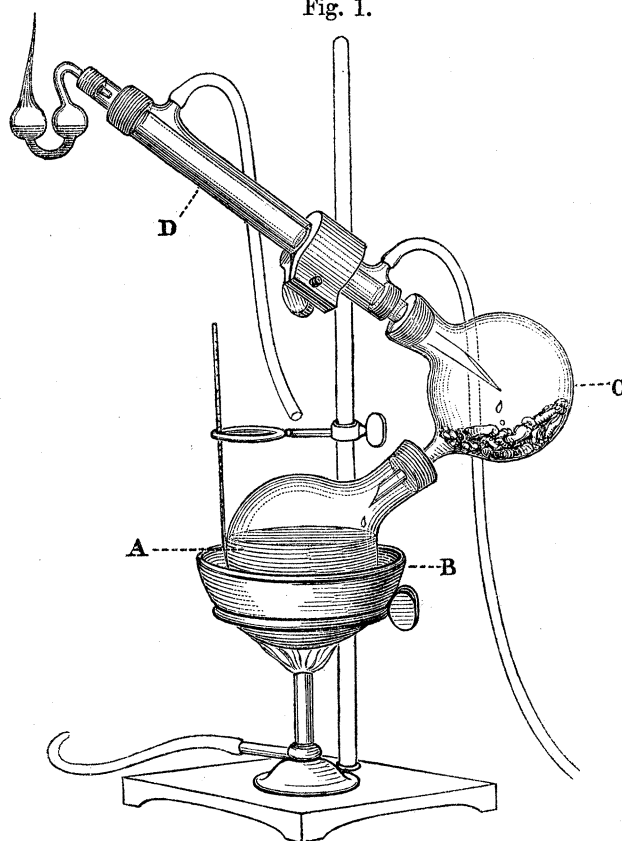
When acetic ether thus prepared is placed in contact with sodium it becomes hot, and a considerable quantity of gas is evolved, which, after being passed first through alcohol and then through water, burns with a non-luminous flame, and the products of combustion do not produce the slightest turbidity on agitation with baryta-water. In fact the gas is pure hydrogen. When the action is complete, the liquid solidifies on cooling to a mass resembling yellow beeswax. By putting the sodium into the acetic ether as just described, it is difficult to conduct the operation to completion, owing to the liquid gradually assuming such a thick and pasty condition as to prevent the further action of the sodium. We therefore adopted the following modification, which enabled us to push the reaction almost to its extreme limit.

A (fig. 1) is a flask containing the acetic ether, and standing in an oil-bath, B. The neck of the flask was closed with a caoutchouc cork, through which passed the beak of the quilled receiver C, containing the sodium cut up into pieces about 1 inch square and  $\frac{1}{4}$  inch thick. Into the wide neck of this receiver was inserted an inverted LIEBIG'S condenser, D, which projected sufficiently into the vessel to allow the condensed liquid to drip back upon the sodium. Heat being applied to the oil-bath, the acetic ether soon began to boil, and by its condensation in C and D not only kept the surface of the sodium constantly moist with fresh portions of acetic ether, but also dissolved off the solid sodium-compound as fast as formed. As the operation progressed it was found necessary to raise the temperature of the oil-bath, so as to cause the continuous distillation of the remaining acetic ether, which acquired a higher boiling-point as the pro-

\* Methylated spirit may be used for this purpose.

portion of sodium-compound dissolved in it increased; but the temperature ought not to be allowed to rise above  $130^{\circ}\text{C}$ . When the acetic ether ceases to distil at this temperature, the proportion of sodium dissolved is not much below one atom for each atomic proportion of acetic ether employed, and it was not found advantageous to push the reaction further. The contents of the flask were now submitted to the action of ethyl iodide, for which purpose they were transferred whilst still liquid to an iron digester, and mixed with a quantity of ethyl iodide equivalent to the amount of sodium dissolved. The digester was then exposed to a temperature of  $100^{\circ}\text{C}$  bath for several hours, and after being allowed to cool, water in consi introduced, and the whole submitted to distillation in an oil-bath. over a large quantity of ethylic ether mixed with some acetic ether

Fig. 1.



decomposition. As the temperature in the interior of the digester rose above  $100^{\circ}$ , the distillate began to separate into an aqueous and an ethereal portion, and further quantities of water were repeatedly added until no more ethereal liquid distilled. The ethereal, separated from the aqueous portion, presented the appearance of a light straw-coloured oil, possessing a pleasant and fragrant odour. It was washed with water, then dried over calcium chloride, and submitted to fractional distillation, by which traces of alcohol, acetic ether, and ethyl iodide were effectually removed from the other products,

which now boiled between  $120^{\circ}$  and  $265^{\circ}$  C. It will be most convenient to describe the constituents of this complex liquid under two distinct heads, viz.—

1st. Products depending upon the duplication of the atom of acetic ether.

2nd. Products derived from the replacement of hydrogen in the methyl of acetic ether by the alcohol-radicals.

In order successfully to separate the two products from each other, and especially to disentangle their constituent compounds, it is absolutely necessary to operate upon large quantities of material. But if this be done, there is obtained a considerable quantity of the products of the first division boiling between  $204^{\circ}$  and  $208^{\circ}$  C., whilst the products of the second division boil considerably below these temperatures.

*α. Examination of the products depending upon the duplication of the atom of acetic ether.*

Submitted to analysis, this liquid gave the following numbers:—

I. .3920 grm. gave .9010 grm. carbonic acid and .3291 grm. water.

II. .2772 grm. gave .6347 grm. carbonic acid and .2338 grm. water.

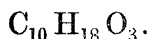
These numbers agree very closely with the formula



as the following comparison shows:

Calculated.		Found.		
		I.	II.	Mean.
$\text{C}_9$	. . 108      62.79	62.75	62.45	62.60
$\text{H}_{16}$	. . 16      9.22	9.33	9.37	9.35
$\text{O}_3$	. . 48      27.99			
	<hr/> 172      100.00			

In addition to this very close correspondence between the experimental and calculated values, a vapour-density determination gave the number 6.001, the above formula requiring 5.94; nevertheless the body in question is not a single substance, for after being boiled for several hours with aqueous potash, its boiling-point rose to between  $210^{\circ}$  and  $212^{\circ}$ , and on being again submitted to analysis it gave results required by the formula

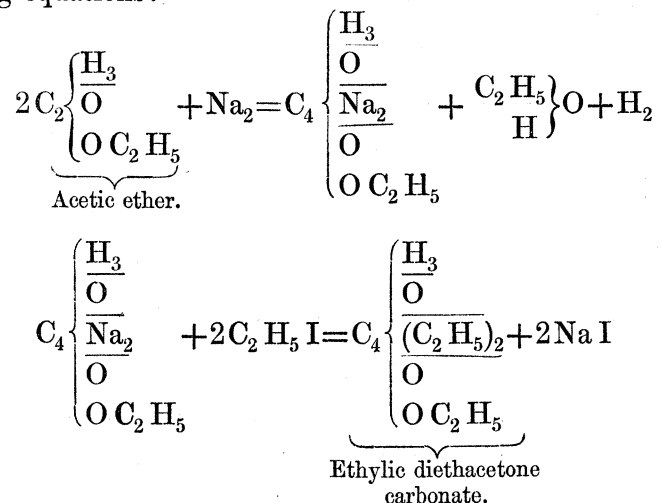


I. .2626 grm. gave .6184 grm. carbonic acid and .2308 grm. water.

II. .3339 grm. gave .7896 grm. carbonic acid and .2924 grm. water.

Calculated.		Found.		
		I.	II.	Mean.
$\text{C}_{10}$	. . 120      64.52	64.22	64.49	64.36
$\text{H}_{18}$	. . 18      9.68	9.77	9.73	9.75
$\text{O}_3$	. . 48      25.80			
	<hr/> 186      100.00			

From considerations which are fully entered into below, we propose for this body the name *ethylic diethacetone carbonate*. The formation of this compound is explained in the following equations:—



Ethylic diethacetone carbonate is a colourless and somewhat oily liquid, possessing a fragrant odour and a pungent taste. It is insoluble in water, but miscible in all proportions with alcohol or ether. Its specific gravity is ·9738 at 20° C. It boils between 210° and 212°, and distils unchanged. The density of its vapour was calculated from the following numbers to be 6·59.

Weight of liquid . . . . .	·1978 gramm.
Observed volume of vapour . . . . .	46·01 cub. centims.
Temperature of bath . . . . .	232° C.
Height of barometer . . . . .	767 millims.
Difference of heights of mercury inside and outside tube . .	76·5 millims.
Height of spermaceti column reduced to millims. of mercury	15·1 millims.

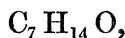
The above formula, corresponding to two volumes, requires the number 6·43.

Boiling aqueous solutions of potash and soda have scarcely any action on ethylic diethacetone carbonate, but baryta-water and lime-water decompose it with great facility, as do also boiling alcoholic solutions of potash and soda. In all these cases a carbonate of the base is precipitated, whilst alcohol and a light ethereal liquid are produced.

This liquid, freed from alcohol by repeated washing with salt and water, boiled, after drying over calcium chloride, between 137°·5 and 139° C. Submitted to analysis, it yielded the following results:

·2075 gramm. gave ·5594 gramm. carbonic acid and ·2313 gramm. water.

These numbers agree with the formula



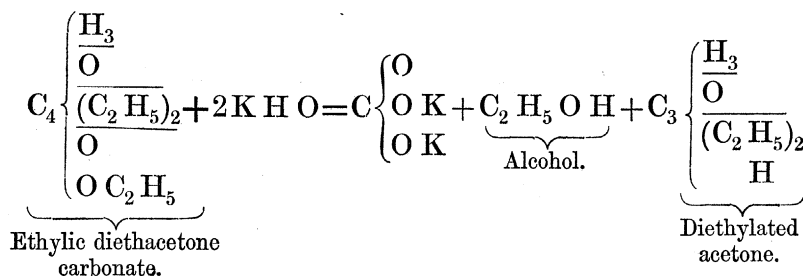
as seen from the following comparison:

	Calculated.		Found.
C <sub>7</sub> . . .	84	73·68	73·52
H <sub>14</sub> . . .	14	12·28	12·38
O . . .	16	14·04	
	114	100·00	

From the mode of its formation, and its analogy with other similar bodies described below, this ethereal liquid must be regarded as a ketone, and we propose for it the name *diethylated acetone*. Its rational formula and its relations to acetone may be thus expressed :



Diethylated acetone is produced from ethylic diethacetone carbonate by the action of alcoholic potash according to the following equation :



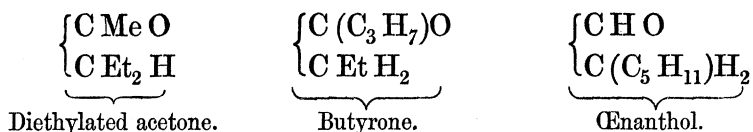
Diethylated acetone is a colourless, transparent and mobile liquid, possessing a penetrating odour of camphor, and the burning and bitter after-taste of the same substance. It is very slightly soluble in water, but miscible in all proportions with alcohol or ether. Its specific gravity is ·8171 at 22° C. It boils at 137°·5 to 139° C. A determination of its vapour-density by GAY LUSSAC'S method gave the following data:—

Weight of diethylated acetone . . . . .	·1930 grm.
Observed volume of vapour . . . . .	62·0 cub. centims.
Temperature of bath . . . . .	161° C.
Height of barometer . . . . .	773 millims.
Difference of heights of mercury inside and outside tube . .	39·5 millims.
Height of spermaceti column reduced to millims. of mercury	15·7 millims.

From these numbers the density was calculated to be 3·86; the formula C<sub>7</sub> H<sub>14</sub> O requires the number 3·93. Diethylated acetone does not oxidize in the air, neither does it reduce ammoniacal solution of silver nitrate when boiled with it. Mixed with concentrated solution of sodium bisulphite, it forms an oily compound which scarcely exhibits signs of crystallization at 0° C. It suffers no alteration by prolonged boiling with alcoholic potash. It is isomeric with butyrene, with a ketone obtained by FITTIG\* in the

\* Ann. der Ch. und Pharm. Bd. cxvii. p. 68.

distillation of a mixture of valeraldehyde and quicklime, and with œnanthol. From the first two it is distinguished by its lower boiling-point ( $138^{\circ}$ ), butyrone boiling at  $144^{\circ}$  C., and FITTIG's ketone at  $161^{\circ}$  to  $164^{\circ}$ , and from the third by its different properties, which are essentially those of a ketone and not of an aldehyde. The difference in structure of three of these bodies may be expressed with considerable certainty by the following formulæ:—

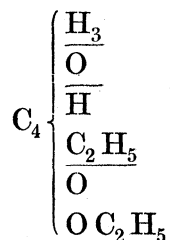


We have mentioned above that ethylic diethacetone carbonate is freed from another body with which it is associated, by long ebullition with aqueous potash. A large quantity of potassium carbonate is formed in this reaction, and there is at the same time a volatile body of a ketonic character set free. This led us to suspect the presence in the original mixture of a lower homologue formed by the action of only one atom of sodium upon two atoms of acetic ether—a suspicion supported by the composition of the mixture as shown by the analyses given at page 40, which indicate the formula



that would be deduced from the analysis of equal weights of ethylic diethacetone carbonate ( $\text{C}_{10} \text{H}_{18} \text{O}_3$ ), and its lower homologue, ethylic ethacetone carbonate ( $\text{C}_8 \text{H}_{14} \text{O}_3$ ). Further investigation of the mixture before boiling with aqueous potash completely confirmed this surmise; for by careful fractional distillation we succeeded in separating two liquids of constant boiling-point, one of which was ethylic diethacetone carbonate, and the other *ethylic ethacetone carbonate*. The latter yielded on analysis the following numbers. .2411 grm. gave .5387 grm. carbonic acid and .1944 grm. water.

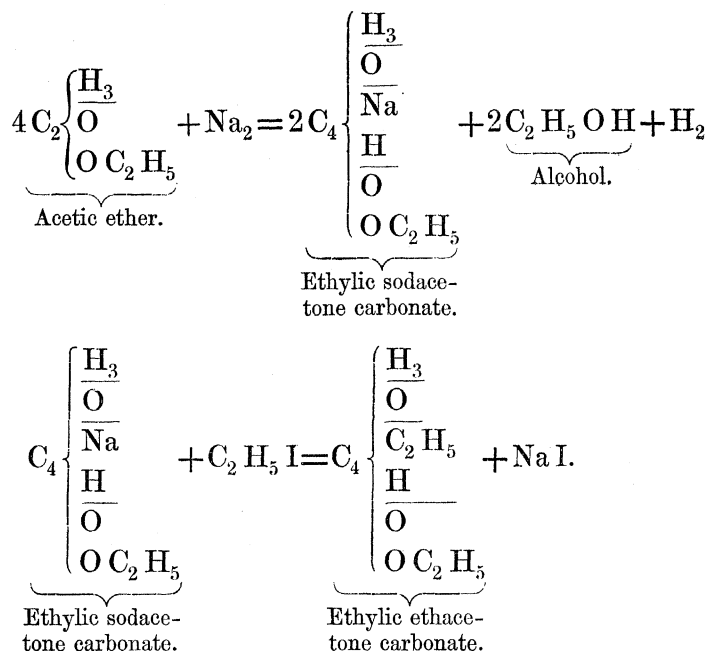
These numbers correspond well with the formula



as is seen from the subjoined comparison:

	Calculated.		Found.
$\text{C}_8$ . . .	96	60.76	60.94
$\text{H}_{14}$ . . .	14	8.86	8.96
$\text{O}_3$ . . .	48	30.38	
	158	100.00	

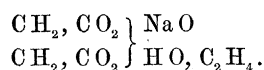
The production of ethylic ethacetone carbonate by the action of sodium and ethyl iodide upon acetic ether is explained in the two following equations\*:



Ethylic ethacetone carbonate is a colourless and transparent liquid, possessing a very fragrant odour and an aromatic taste. It is nearly insoluble in water, but miscible in all proportions with alcohol and ether. Its density in the liquid condition is .9834 at 16° C. It boils at 195° C., and distils without decomposition. A determination of its vapour-density gave the following data:—

Weight of ethylic-ethacetone carbonate . . . . .	·1993 grm.
Observed volume of vapour . . . . .	54·09 cub. centims.
Height of barometer . . . . .	763·5 millims.
Difference of heights of mercury inside and outside tube . . . . .	76·0 millims.
Height of spermaceti column reduced to millims. of mercury . . . . .	15·7 millims.

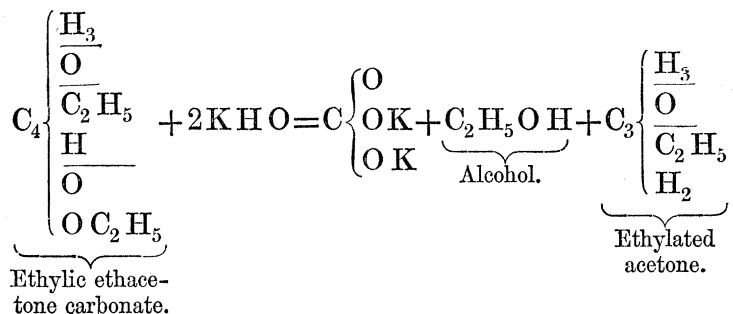
\* Whilst engaged in these experiments we became aware, through the 'Jahresbericht der Chemie,' that this compound, and the corresponding one made with iodide of methyl mentioned below, had already been studied by GEUTHER, who also obtained ethylic sodacetone carbonate, which he analyzed and designated by the name *Di-methylene-carbon-ethylene-sodic ether*, assigning to it the formula (C=12, O=8),



From this body he produced ethylic ethacetone carbonate (*Di-methylene-carbon-ethylene ether*) by the action of ethyl iodide, and also *ethylic methacetone carbonate* (*Di-methylene-carbon-methylene ether*) by the action of methyl iodide. Our analytical results and observations of the physical properties of these two bodies agree completely with those assigned to them by GEUTHER, whose isolation of the sodium-compound, attended as it is with great difficulties, serves to impart a completeness to the reaction which it would otherwise have lacked.



From these numbers the specific gravity was calculated to be 5·36; theory requires 5·45. Ethylic ethacetone carbonate, unlike ethylic-diethacetone carbonate, and in opposition to GEUTHER's statement, is readily attacked by boiling aqueous solutions of potash and soda, yielding carbonates of these bases, alcohol, and *ethylated acetone* according to the following equation:—

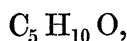


Ethylic ethacetone carbonate is still more readily decomposed by aqueous solution of baryta or by alcoholic potash; in both cases ethylated acetone and a carbonate of the base are produced.

Ethylated acetone may be freed from alcohol by repeated washing with salt and water, but it is best obtained in a state of absolute purity by combination with, and subsequent separation from sodium bisulphite. Ethylated acetone thus purified and rectified from quicklime, gave on analysis the following numbers:—

·1483 gramm. gave ·3799 gramm. carbonic acid and ·1575 gramm. water.

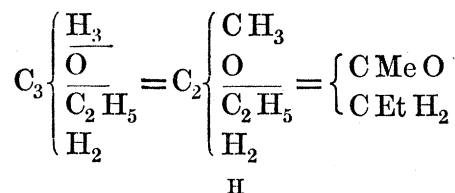
This result agrees well with the formula



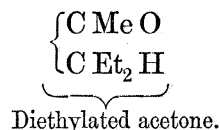
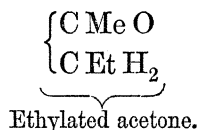
as seen from the following comparison of experimental with theoretical percentage numbers:—

Calculated.		Found.
C <sub>5</sub>	60	69·77
H <sub>10</sub>	10	69·86
O	16	11·63
	86	18·60
		100·00

The formula of ethylated acetone given above may be reduced to the radical type as follows:—



Its relations to acetone and diethylated acetone are then clearly seen in the following formulæ:—



Ethylated acetone is a colourless, transparent and very mobile liquid, possessing a powerful and pleasant odour, in which that of camphor is slightly perceptible. Its specific gravity is  $\cdot 8132$  at  $13^\circ \text{C}$ ., and  $\cdot 8046$  at  $22^\circ \text{C}$ . It boils steadily at  $101^\circ$  (barom. 760 millims.), and its vapour has the density  $2\cdot 951$ , as calculated from the following data, theory requiring  $2\cdot 971$ .

Weight of ethylated acetone . . . . .	$\cdot 1368$ grm.
Observed volume of vapour . . . . .	$55\cdot 64$ cub. centims.
Temperature of bath . . . . .	$124^\circ \text{C}$ .
Height of barometer . . . . .	773 millims.
Difference of heights of mercury inside and outside tube . .	80 millims.
Height of spermaceti column reduced to millims. of mercury	$15\cdot 7$ millims.

Ethylated acetone neither absorbs oxygen from the air, nor reduces ammoniacal solutions of silver. It yields with concentrated solution of sodium bisulphite a compound in large and brilliant crystals, which are quite permanent in the air, and which at once distinguish it from diethylated acetone, the latter producing under the same circumstances an oily compound. Ethylated acetone is not altered by prolonged ebullition with alcoholic potash. Its relations to numerous isomers are described below.

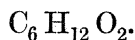
*β. Examination of the products derived from the replacement of hydrogen by ethyl in the methyl of acetic ether.*

This portion of the original product derived from the action of sodium and ethylic iodide upon acetic ether, and which boiled considerably below the portion  $\alpha$ , was submitted to repeated rectifications, and was thus resolved to a great extent into two ethereal liquids, one of them boiling between  $118^\circ$  and  $122^\circ$ , and the other between  $150^\circ$  and  $157^\circ \text{C}$ . On treating these liquids with boiling baryta-water for several hours in order to remove traces of ethylic diethacetone carbonate and ethylic ethacetone carbonate, the point of ebullition of the first was rendered quite constant at  $119^\circ \text{C}$ ., and that of the second at  $151^\circ \text{C}$ .

Submitted to analysis, the first of these liquids yielded the following results:—

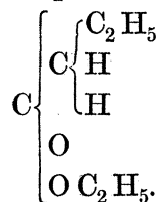
- I.  $\cdot 1716$  grm. gave  $\cdot 3922$  grm. carbonic acid and  $\cdot 1626$  grm. water.
- II.  $\cdot 2190$  grm. gave  $\cdot 5007$  grm. carbonic acid and  $\cdot 2063$  grm. water.

These numbers coincide closely with those calculated from the formula

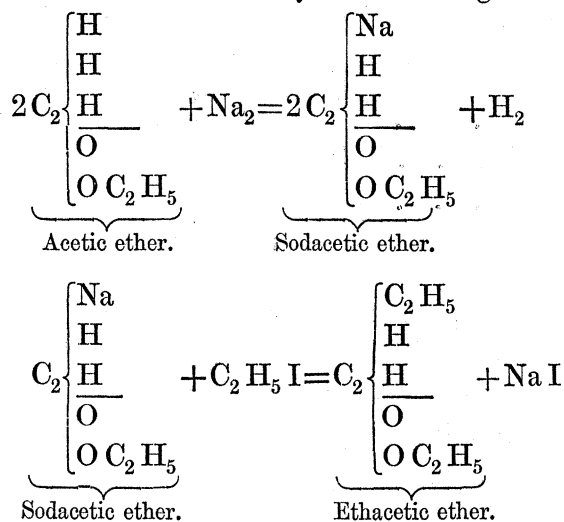


	Calculated.		Found.		
			I.	II.	Mean.
C <sub>6</sub> . . .	72	62·07	62·33	62·35	62·34
H <sub>12</sub> . . .	12	10·35	10·53	10·47	10·50
O <sub>2</sub> . . .	32	27·58			
	116	100·00			

The formula and habits of this compound show it to be *ethacetic ether*:



Ethacetic ether is produced from acetic ether by the following reactions:—

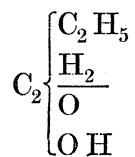


Ethacetic ether possesses all the properties of butyric ether. It is colourless and transparent, and when largely diluted with alcohol possesses the characteristic odour of pine-apples, which is undistinguishable from that of butyric ether under the same circumstances. Its density is ·8942 at 0° C., that of butyric ether being, according to PIERRE, ·9019 at 0° C., numbers which coincide with each other as closely as could be expected. The boiling-point (119° C.) of ethacetic ether also agrees exactly with that of butyric ether given by the same authority, as does the vapour-density, which was ascertained to be 3·96 from the following data, the theoretical number being 4·04.

Weight of ethacetic ether . . . . .	·1769 grm.
Observed volume of vapour . . . . .	57·24 cub. centims.
Temperature of bath . . . . .	148° C.
Height of barometer . . . . .	763·5 millims.
Difference of height of mercury inside and outside tube . . .	75·7 millims.
Height of spermaceti column reduced to millims. of mercury	15·7 millims.

Ethacetic ether is readily decomposed by boiling alcoholic potash, yielding alcohol and a salt which, when distilled with slight excess of dilute sulphuric acid, gives a powerfully acid oily liquid, tolerably soluble in water, possessing in a high degree the characteristic odour of butyric acid, and boiling fixedly at  $161^{\circ}\text{C}$ . The boiling-point of butyric acid has been variously stated by different observers: PELOUZE and GELIS state it to be  $164^{\circ}$ , whilst KOPP gives it as  $157^{\circ}$  at 760 millims. pressure.

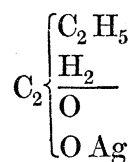
Submitted to analysis,  $\cdot 2439$  gram. *ethacetic acid* gave  $\cdot 4862$  gram. carbonic acid and  $\cdot 2030$  gram. water, numbers which correspond with the formula



The following is a comparison of the analytical with the calculated numbers:—

	Calculated.		Found.
C <sub>4</sub> . . .	48	54·54	54·37
H <sub>8</sub> . . .	8	9·09	9·25
O <sub>2</sub> . . .	32	36·37	
	<hr/> 88	<hr/> 100·00	

Boiled with water and silver carbonate, ethacetic acid yields, after some hours, a crop of beautiful ramiform needle-like crystals, aggregated into large globular masses, which become anhydrous *in vacuo*; both the mother-liquor and crystals have a faint smell of rancid butter. Submitted to analysis, these crystals yielded results agreeing with the formula for silver ethacetate,



$\cdot 2738$  gram. gave  $\cdot 2463$  gram. carbonic acid,  $\cdot 0889$  gram. water, and  $\cdot 1518$  gram. silver.

	Calculated.		Found.
C <sub>4</sub> . . .	48	24·61	24·53
H <sub>7</sub> . . .	7	3·59	3·61
Ag . . .	108	55·38	55·44
O <sub>2</sub> . . .	32	16·42	
	<hr/> 195	<hr/> 100·00	

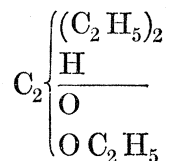
We have been unable to detect any difference between ethacetic acid and butyric acid, and we have stated below our reasons for believing them to be identical.

The second portion of the product  $\beta$ , mentioned above as a liquid boiling at  $151^{\circ}\text{C}$ ., was next submitted to analysis.

I. .2276 grm. gave .5523 grm. carbonic acid and .2279 grm. water.

II. .1839 grm. gave .4461 grm. carbonic acid and .1847 grm. water.

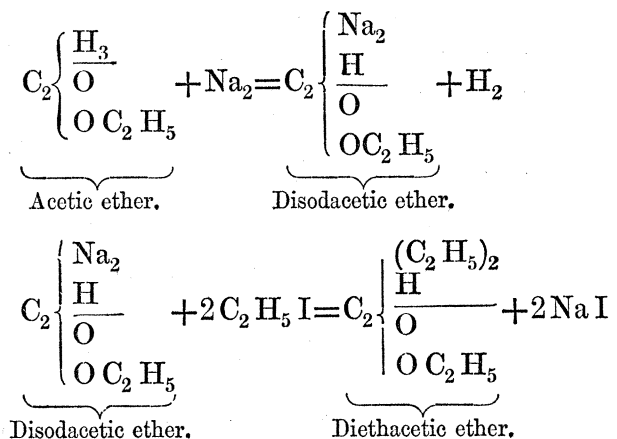
These results correspond with the formula of *diethacetic ether*,



as is seen from the following comparison:—

Calculated.				Found.	
				I.	II.
$\text{C}_8$	. . .	96	66.66	66.18	66.16
$\text{H}_{16}$	. . .	16	11.11	11.13	11.16
$\text{O}_2$	. . .	32	22.23		
		144	100.00		

Diethacetic ether is derived from acetic ether by the following reactions:—



Diethacetic ether is a colourless and transparent liquid of a peculiar and fragrant odour, and a taste somewhat like peppermint. Its specific gravity is .8822 at  $0^{\circ}\text{C}$ . It is insoluble in water, but miscible in all proportions with alcohol and ether. It boils constantly at  $151^{\circ}\text{C}$ ., and its vapour has, theoretically, the density 4.98. Experimentally the number 5.00 was obtained from the following data:—

Weight of diethacetic ether . . . . .	.1697 grm.
Observed volume of vapour . . . . .	48.23 cub. centims.
Temperature of bath . . . . .	$168^{\circ}\text{C}$ .
Height of barometer . . . . .	758 millims.
Difference of heights of mercury inside and outside tube . .	109 millims.
Height of spermaceti column reduced to millims. of mercury	15.7 millims.

Treated with alcoholic potash, diethacetic ether is readily decomposed, yielding alcohol and potassium diethacetate. By distilling the latter with dilute sulphuric acid, diethacetic acid passes over and floats on the surface of the water which accompanies it. This acid reddens litmus-paper powerfully, is but sparingly soluble in water, and emits a peculiar odour quite different from that of caproic acid, with which diethacetic acid is isomeric. Boiled with water and silver carbonate, it yields, on filtration and evaporation *in vacuo*, splendid fern-like crystals, which, after pressing between folds of blotting-paper and drying *in vacuo*, with the exclusion of light, are perfectly white, with a satiny lustre; they possess great elasticity, and are remarkably like asbestos. In a strong light they rapidly become brown. Submitted to analysis,

·1990 grm. gave ·2325 grm. carbonic acid, ·0902 grm. water, and ·0980 grm. metallic silver.

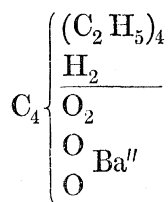
These numbers agree with the formula

$$\text{C}_2 \left\{ \begin{array}{l} (\text{C}_2 \text{H}_5)_2 \\ \text{H} \\ \text{O} \\ \text{O Ag} \end{array} \right.$$

		Calculated.	Found.
C <sub>6</sub>	. . . 72	32·28	31·86
H <sub>11</sub>	. . . 11	4·93	5·04
Ag	. . . 108	48·43	49·25
O <sub>2</sub>	. . . 32	14·36	13·85
	223	100·00	100·00

Barium diethacetate is very soluble in water, and on evaporation forms a beautifully crystalline mass.

A determination of barium in this salt yielded 38·05 per cent.; the formula



requires 37·33 per cent. of barium.

Diethacetic acid differs markedly from caproic acid in its odour, as above mentioned, whilst the compounds of the two acids scarcely permit of their being confounded with each other. Thus diethacetic ether differs from caproic ether by 11° in its boiling-point, which is 151° C., the boiling-point of caproic ether being, according to FEHLING, 162°. In their specific gravities also the two ethers appreciably differ, caproic ether having a density of ·882 at 18° C., whilst the specific gravity of diethacetic ether is ·8822 at 0° C. The silver salts differ widely in their crystalline form, solubility in water, and sensitiveness

to the influence of light. Silver caproate crystallizes in large and very thin plates, which are nearly insoluble in water and but very slightly sensitive to light, whilst silver dieth-acetate is deposited in frond-like crystals, which are quite as soluble as silver acetate, and become rapidly brown when exposed to light. We therefore conclude that these acids are isomeric and not identical. Theoretical considerations leading to the same conclusion are given below.

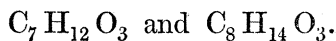
*Action of Sodium and Methyl Iodide upon Acetic Ether.*

Acetic ether was treated with sodium, as in the corresponding reaction described above; but in the subsequent treatment of the sodium-compound it was not found necessary to expose the mixture of the latter with methyl iodide to heat in a digester. These materials act upon each other with great energy and completeness at a temperature below the boiling-point of methyl iodide. At the conclusion of the sodium-reaction, therefore, the temperature was allowed to fall until the liquid in the flask began to solidify, and the receiver, C (see figure, p. 39), with the residue of sodium being removed, the extremity of the condenser was inserted into the neck of the flask. Methyl iodide in excess was then slowly added by pouring it down the condenser. An energetic action immediately took place, a large quantity of sodium iodide being formed. To complete this reaction, one atom of methyl iodide for each atom of sodium employed was found to be sufficient. The ethereal part of the product in the flask now remained liquid, even after cooling, the sodium iodide subsiding as a dense precipitate. Water was then added, and the contents of the flask submitted to distillation. Water, alcohol, and an oily liquid which floated on the aqueous portion of the distillate, condensed in the receiver. When the oily liquid ceased to come over, the contents of the retort were slightly acidified with dilute sulphuric acid, more water added, and the distillation continued into a fresh receiver. The acid distillate thus obtained did not contain any formic acid, and consisted chiefly of acetic acid, with traces of other higher acids belonging to the same series.

The aqueous portion of the distillate was separated from the oily, and submitted to distillation in an oil-bath. A considerable quantity of a spirituous liquid passed over, which, after rectification from quicklime, boiled at  $78^{\circ}5$ , and consisted of pure alcohol. It yielded on combustion 52.29 per cent. of carbon and 12.98 per cent. of hydrogen. Alcohol requires 52.17 per cent. of carbon and 13.04 per cent. of hydrogen.

The oily portion of the distillate was repeatedly washed with water, dried over calcium chloride, and rectified. It began to boil at  $75^{\circ}$ , but the thermometer rapidly rose to  $183^{\circ}$ , between which temperature and  $184^{\circ}$  nearly the whole of the remaining large portion of liquid came over.

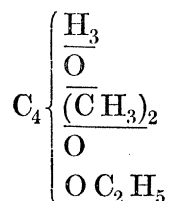
Notwithstanding the constancy of boiling-point of this liquid, numerous analyses showed it to be a mixture, and the numbers obtained were consistent with the assumption that it was composed of two bodies having respectively the formulæ



In fact it was evident that the liquid with which we had now to do was the exact counterpart of the one obtained in the corresponding reaction with ethyl iodide described above, and that it consisted of the homologues produced in the ethylic reaction, viz. *ethylic methacetone carbonate* and *ethylic dimethacetone carbonate*. To separate these compounds, whose boiling-points were evidently nearly if not absolutely identical, we availed ourselves of their different behaviour with boiling aqueous potash; ethylic dimethacetone carbonate, like ethylic diethacetone carbonate, being scarcely affected by this treatment, whilst ethylic methacetone carbonate, like its ethylic homologue, is rapidly decomposed. By thus boiling several ounces of the mixed ethers with aqueous potash, a liquid was obtained which, by repeated rectification, was separated into two products, the one boiling at about 80° C., and the other constantly at 184° C. The latter was submitted to analysis, and yielded the following results:—

- I. .2001 grm. gave .4435 grm. carbonic acid and .1598 grm. water.
- II. .1647 grm. gave .3652 grm. carbonic acid and .1317 grm. water.
- III. .3040 grm. gave .6728 grm. carbonic acid and .2399 grm. water.
- IV. .2739 grm. gave .6052 grm. carbonic acid and .2218 grm. water.
- V. .3319 grm. gave .7388 grm. carbonic acid and .2721 grm. water.
- VI. .2548 grm. gave .5686 grm. carbonic acid and .2075 grm. water.

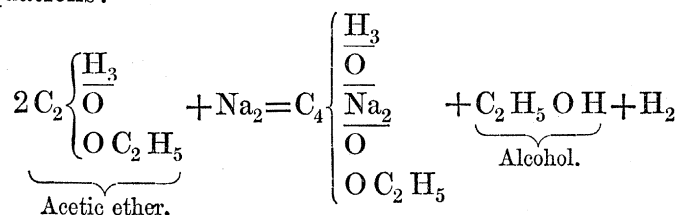
These numbers approximate closely to those required by the formula of ethylic dimethacetone carbonate,



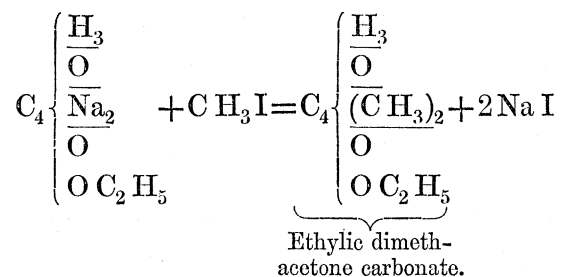
as shown by the following comparison:—

Calculated.			Found.						
			I.	II.	III.	IV.	V.	VI.	Mean.
C <sub>8</sub>	. 96	60·76	60·45	60·47	60·36	60·26	60·71	60·86	60·52
H <sub>14</sub>	. 14	8·86	8·87	8·88	8·77	9·00	9·11	9·05	8·95
O <sub>3</sub>	. 48	30·38							
	158	100·00							

The production of ethylic dimethacetone carbonate from acetic ether is explained by the following equations:—







Ethylic dimethacetone carbonate is a colourless, slightly oleaginous liquid, possessing a peculiar penetrating pleasant and aromatic odour, and a sharp burning taste. It is scarcely at all soluble in water, but readily so in alcohol or ether. Its specific gravity is .9913 at 16° C. It boils constantly at 184°, and distils unchanged. A determination of its vapour-density gave the following numbers:—

Weight of ethylic dimethacetone carbonate . . . . .	.1993 gramm.
Observed volume of vapour . . . . .	54.09 cub. centims.
Temperature of bath . . . . .	194° C.
Height of barometer . . . . .	763.5 millims.
Height of internal column of mercury . . . . .	76.0 millims.
Height of column of spermaceti 253 millims. reduced to } millims. of mercury . . . . . }	15.7 millims.

From these data the specific gravity of the vapour was calculated to be 5.36. The above formula, corresponding to two volumes, requires 5.45.

Ethylic dimethacetone carbonate is very slowly acted upon by aqueous solution of potash or soda. A quantity of it was boiled, without any perceptible diminution of its volume, with two separate portions of strong solution of potash for eight or ten hours, an inverted condenser being attached to the flask.

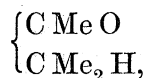
Alcoholic potash in the cold decomposes it very slowly, but when heated to boiling complete decomposition is effected in a very short time. The action is the same as that of baryta-water.

Baryta-water instantly attacks ethylic dimethacetone carbonate in the cold, barium carbonate being immediately precipitated. At 100° C. the decomposition is complete in a few minutes; and on submitting the mixture to distillation, alcohol and a light ethereal liquid pass over. The latter, repeatedly washed with a saturated solution of common salt to remove alcohol, and dried over quicklime, gave on analysis the following numbers:—

- I. .2083 gramm. gave .5301 gramm. carbonic acid and .2220 gramm. water.
- II. .2594 gramm. gave .6572 gramm. carbonic acid and .2728 gramm. water.

When the mode of its formation is considered, these results show that the body analyzed is *dimethylated acetone*, the true homologue of diethylated acetone, and the isomer of ethylated acetone.

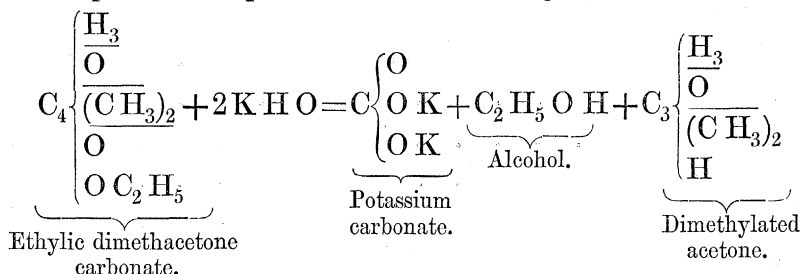
The percentage numbers calculated from its formula,



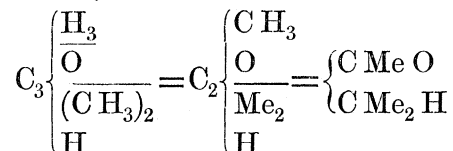
agree with those obtained in the above analyses.

		Calculated.		Found.		
				I.	II.	Mean.
C <sub>5</sub>	. .	60	69.77	69.41	69.10	69.26
H <sub>10</sub>	. .	10	11.63	11.84	11.68	11.76
O	. .	16	18.60			
		86	100.00			

The production of dimethylated acetone from ethylic dimethacetone carbonate by the action of alcoholic potash is explained in the following equation:—



The above formula for dimethylated acetone is condensed to the radical type as follows:—



Dimethylated acetone is a colourless, transparent and very mobile liquid, possessing a pleasant odour, reminding at the same time of parsley and acetone. Its specific gravity is .8099 at 13° C., and it boils at 93°·5 C. A determination of its vapour-density gave the following numbers:—

Weight of dimethylated acetone . . . . .	.1378 gm.
Observed volume of vapour . . . . .	58.00 cub. centims.
Temperature of bath . . . . .	120° C.
Height of barometer . . . . .	744 millims.
Difference of heights of mercury inside and outside tube . .	75 millims.
Height of spermaceti column reduced to millimetres of mercury	15.3 millims.
Specific gravity of vapour . . . . .	2.92
Theoretical density calculated from C <sub>5</sub> H <sub>10</sub> O=2 vols. . . .	2.97

Dimethylated acetone closely resembles its ethylic homologue in all its chemical properties; like diethylated acetone, it is oxidized with difficulty, and does not very readily form a crystalline compound with sodium bisulphite—differing in the latter respect markedly from its isomer, ethylated acetone, and also from methylated acetone described below.

We have mentioned above that the ethereal liquid from which ethylic dimethacetone carbonate was obtained by ebullition with aqueous potash, contained another body probably homologous with ethylic ethacetone carbonate. The following analyses of the ethereal liquid before ebullition with aqueous potash indicate the presence of this body, which may be appropriately named *ethylic methacetone carbonate*. These analyses were made with the products of several distinct operations.

- I. 4248 grm. gave 9289 grm. carbonic acid and 3316 grm. water.  
 II. 3008 grm. gave 6580 grm. carbonic acid and 2364 grm. water.  
 III. 2644 grm. gave 5774 grm. carbonic acid and 2104 grm. water.

The following are the percentage results of these analyses:—

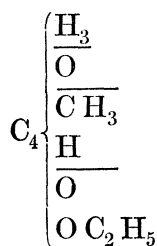
	I.	II.	III.	Mean.
C . .	59.64	59.66	59.56	59.62
H . .	8.67	8.73	8.84	8.75

These numbers coincide very closely with those that would be obtained by the analysis of a mixture of equal weights of ethylic dimethacetone carbonate ( $C_8H_{14}O_3$ ) and ethylic methacetone carbonate ( $C_7H_{12}O_3$ ), viz.,

C . . .	59.54
H . . .	8.60

All attempts to separate these two liquids by fractional distillation failed, owing to the close approximation, if not absolute identity, of their boiling-points. In one operation, however, where the action of sodium upon the acetic ether had not been pushed so far, we obtained a product which consisted almost entirely of ethylic methacetone carbonate, as is seen from the following analysis:—

2624 grm. gave 5637 grm. carbonic acid and 2017 grm. water, numbers which approach closely to the formula of ethylic methacetone carbonate.



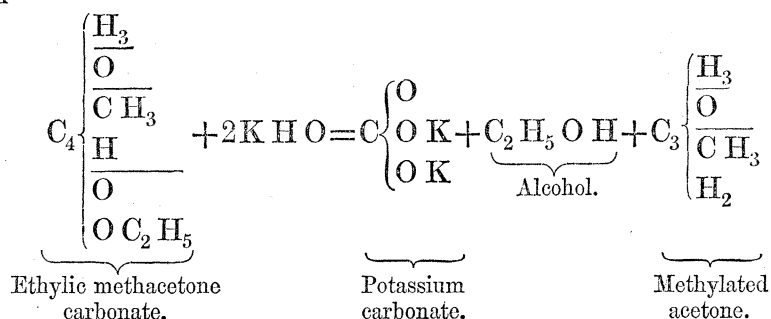
	Calculated.		Found.
C <sub>7</sub> . .	84	58.33	58.59
H <sub>12</sub> . .	12	8.33	8.54
O <sub>3</sub> . .	48	33.34	
	144	100.00	

Finding that this body had been already obtained in a state of perfect purity by GEUTHER\*, we did not make any further attempts to separate it more completely from ethylic dimethacetone carbonate, especially as its presence in the mixtures above ana-

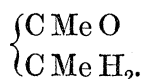
\* Götting. Anzeigen, 1863, p. 281; and Jahresbericht der Chemie, 1863, p. 323.

lyzed is proved by the isolation of methylated acetone—its derivative ketone, as described below.

To the properties of ethylic methacetone carbonate described by GEUTHER, we have only to add that, in opposition to this chemist's statement, it is very readily decomposed by aqueous potash, with the formation of *methylated acetone* according to the following equation:—



Condensed to the radical type, the formula of methylated acetone becomes



Methylated acetone is best obtained in a state of purity by combining it with sodium bisulphite, pressing the beautiful crystalline compound so formed between folds of blotting-paper to remove traces of dimethylated acetone, exposing it over sulphuric acid *in vacuo*, and then regenerating the methylated acetone by distillation with aqueous potash. The liquid so obtained, after drying over quicklime and rectification, gave the following analytical results:—

I. ·1946 grm. gave ·4759 grm. carbonic acid and ·1981 grm. water.

II. ·1461 grm. gave ·3557 grm. carbonic acid and ·1504 grm. water.

These numbers agree well with the above formula.

Calculated.		Found.		
		I.	II.	Mean.
C <sub>4</sub> . . .	48    66·66	66·69	66·40	66·55
H <sub>8</sub> . . .	8    11·11	11·31	11·44	11·37
O . . .	16    22·23			
	<hr/> 72    100·00			

Methylated acetone is a colourless, transparent, and very mobile liquid, possessing an odour like chloroform, but more pungent. It is tolerably soluble in water, and more than slightly so in a saturated solution of common salt. Its specific gravity is ·8125 at 13° C. It boils at 81° C., and its vapour-density is 2·52, as given by the following data, the theoretical number being 2·49.

Weight of methylated acetone . . . . .	·1166 grm.
Observed volume of vapour . . . . .	55·39 cub. centims.
Temperature of bath . . . . .	112° C.
Height of barometer . . . . .	757 millims.

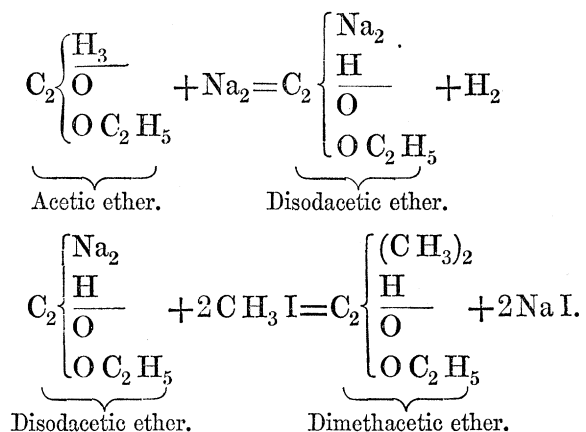
Difference of heights of mercury inside and outside of tube 83·5 millims.

Height of spermaceti column reduced to millims. of mercury 15·7 millims.

We give below our reasons for concluding that methylated acetone is identical with the ethyl-acetyl described by FREUND\*, and obtained by acting upon acetyl chloride with zinc ethide.

Methylated acetone forms a splendidly crystalline compound with sodium bisulphite, and in its other chemical properties so closely resembles ethylated acetone as to require no further description. It retains alcohol with such tenacity as to render its separation from that liquid, by washing and treatment with calcium chloride, almost impossible. This separation, however, is readily effected by the action of sodium bisulphite.

We reserve for a future communication the description of the products derived from the replacement of hydrogen, in the methyl of acetic ether, by methyl; but we may mention before leaving the reaction now under consideration, that we have obtained an ether isomeric with butyric ether, the formation of which is explained in the following equations:—

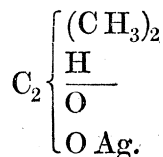


By acting upon this ether with alcoholic potash it is decomposed, yielding alcohol and potassium dimethacetate. On distilling the latter with dilute sulphuric acid, dimethacetic acid, isomeric with butyric acid, is obtained as an oily liquid tolerably soluble in water. Treated with silver carbonate, it readily gave a crystalline silver-salt, which after being well-washed with water and then dried *in vacuo*, yielded the following results on analysis:—

I. ·3920 grm. gave ·3505 grm. carbonic acid, ·1287 grm. water, and ·2172 grm. metallic silver.

II. ·3837 grm. gave ·3399 grm. carbonic acid, ·1246 grm. water, and ·2135 grm. metallic silver.

These numbers agree well with the formula of silver dimethacetate.



\* Ann. der Ch. und Pharm. Bd. cxviii. s. 1.

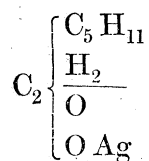
	Calculated.		Found.		Mean.
			I.	II.	
C <sub>4</sub> . . .	48	24·61	24·38	24·16	24·27
H <sub>7</sub> . . .	7	3·59	3·65	3·61	3·63
Ag . . .	108	55·38	55·41	55·64	55·52
O <sub>2</sub> . . .	32	16·42			16·58
	195	100·00			100·00

*Action of Sodium and Amylic Iodide upon Acetic Ether.*

For this reaction the compounds of sodium derived from acetic ether were prepared as before, and were then submitted to the action of amylic iodide for several hours at the boiling-point of the mixture. When the sodium had all become converted into iodide, water was added and the supernatant liquid decanted. We reserve a complete description of this liquid for our next communication, and will here confine ourselves to the separation from it of œnanthylic acid, which was obtained as follows:—The crude product, after drying over calcium chloride, was submitted to rectification, and the portion boiling between 170° and 190° C. collected apart and decomposed by ebullition with alcoholic potash. By this treatment we destroyed any ethylic amylacetone carbonate and ethylic diamylacetone carbonate that were present, and obtained a potash-salt of an acid derived from acetic acid by the substitution of one atom of amyl for one of hydrogen. The potash-salt thus formed was distilled with excess of sulphuric acid diluted with a large quantity of water. Upon the distillate there floated an oily acid, possessing an odour resembling œnanthylic acid. This acid was converted into an ammonia-salt, from which a silver-salt was prepared by precipitation. After being well washed with cold water, this salt yielded the following numbers on analysis:—

·2423 grm. gave ·3159 grm. carbonic acid, ·1204 grm. water, and ·1108 grm. silver.

These numbers agree well with the formula of silver amylacetate or œnanthylate.



	Calculated.		Found.
C <sub>7</sub> . . .	84	35·44	35·56
H <sub>13</sub> . . .	13	5·49	5·52
Ag . . .	108	45·57	45·72
O <sub>2</sub> . . .	32	13·50	13·20
	237	100·00	100·00

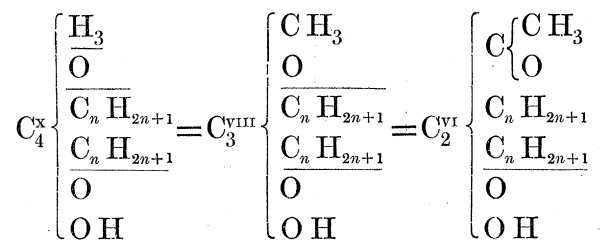
We have also examined the barium-salt, which is an amorphous soapy substance. Dried at 100° C., ·2715 grm. gave ·1599 grm. barium sulphate, corresponding to 34·62

per cent. of barium. Barium ænanthylate contains 34.69 per cent. of barium. We state our reasons below for believing amylic acid to be identical with ænanthylic acid.

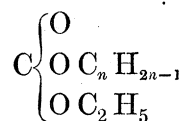
In the foregoing pages we have confined ourselves, as far as possible, to the bare description of experimental results, avoiding any digression to the theoretical considerations which naturally forced themselves upon our attention. It now becomes necessary, however, to take a retrospect of our results, in order to assign to them their proper place amongst chemical phenomena, and to point out their possible bearing upon future investigation in the same direction. In doing this it will be most convenient to discuss the subject under two heads, viz. the considerations involved in the production of the carboketonic ethers derived from the duplication of the atom of acetic ether, and secondly, those suggested by the replacement of the hydrogen in the methyl of acetic ether by the alcohol radicals.

I. *Constitution and chemical relations of the ethers and ketones derived from the duplication of the atom of acetic ether.*

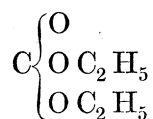
There is always a difficulty in assigning to an entirely new series of organic bodies their true position among other families, and this is more especially the case when, like the bodies now under consideration, they exhibit but few obvious relations to other series. It is therefore with some hesitation, in regard to the ultimate place that may be assigned to them, that we have ventured to consider these bodies as the ethers of peculiar acids, the latter compounded of the ketones and carbonic acid, the general formula of these acids being



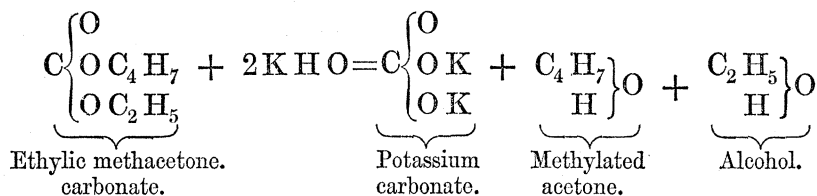
Looking only to the results of the action of caustic alkalies upon the ethylic ethers of these acids, and assuming a formula that will most readily explain this action, we arrive at the following very simple expression for these ethers,



This is obviously the formula of carbonic ether,

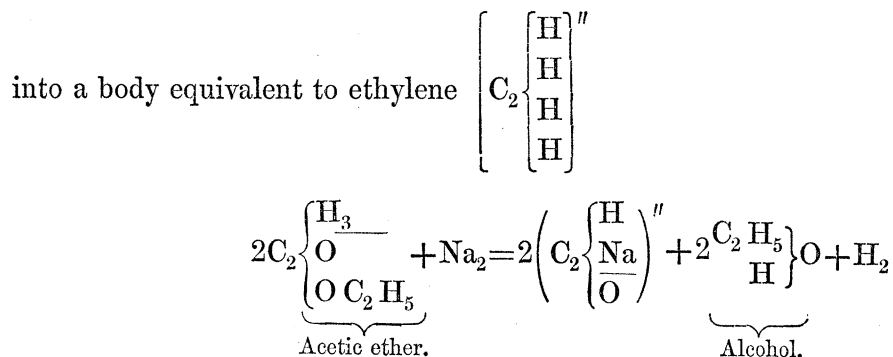


in which one atom of ethyl is replaced by the radical  $C_n H_{2n-1}$ , belonging to the allyl series; and the action of caustic alkalies upon ethylic methacetone carbonate, for instance, would be expressed as follows:—

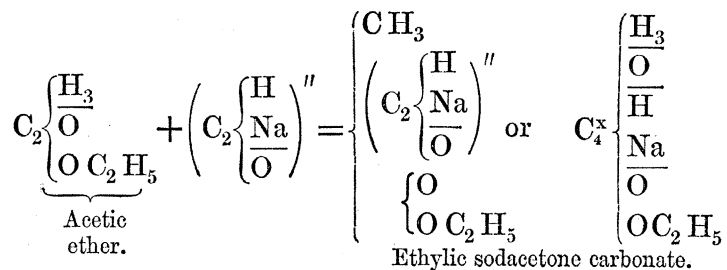


Notwithstanding the very simple expression which is thus given to this reaction, and which is in harmony with KANE'S views of the constitution of acetone, we cannot adopt it without complicating other well-marked reactions in the ketone family, and ignoring the very palpable difference between the ketonic and alcoholic families. This alcoholic side of the ketone character, if we may be allowed the expression, supported as it is by the numerous compounds described by KANE, merits more attention than has hitherto been bestowed upon it, and on this account we have drawn attention to its bearings upon the bodies now under discussion, although we have not been able, in its present aspect, to avail ourselves of it in the interpretation of the reactions now under consideration.

In the rational formulæ which we have adopted for the carboketonic ethers, it is not difficult to trace the two original atoms of acetic ether which give rise to the new bodies. To take the production of ethylic methacetone carbonate as an example, it may be assumed that the action of sodium upon one atom of acetic ether converts the latter

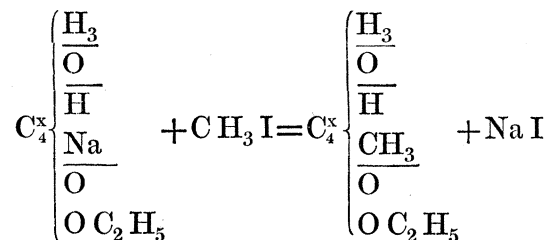


and that this diatomic body then coalesces with an atom of unchanged acetic ether, linking together the two radicals of the latter, thus:

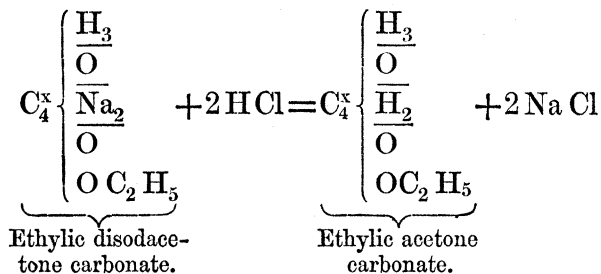
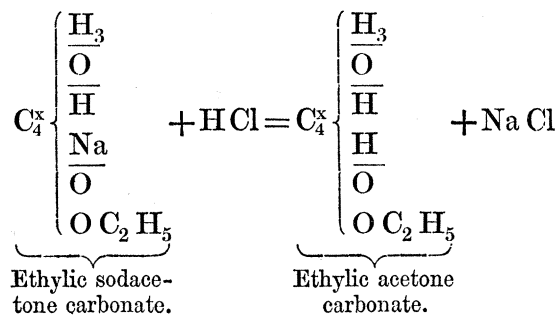




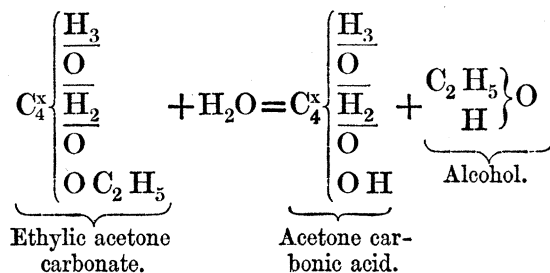
The exchange of sodium for methyl then converts ethylic sodacetone carbonate into ethylic methacetone carbonate.



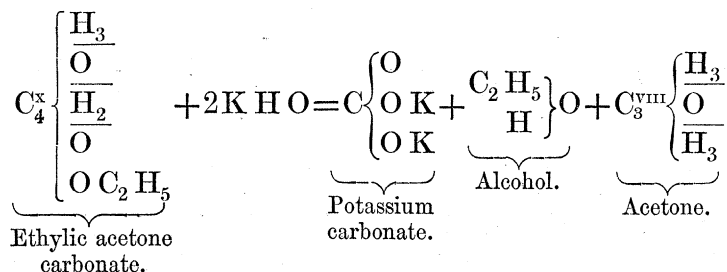
The constitution of the carboketonic ethers here developed indicates the existence of a compound in which the value of  $n$  in the above general formula = 0. Such an ether would be produced by acting with hydrochloric acid upon either ethylic sodacetone carbonate or ethylic disodacetone carbonate.



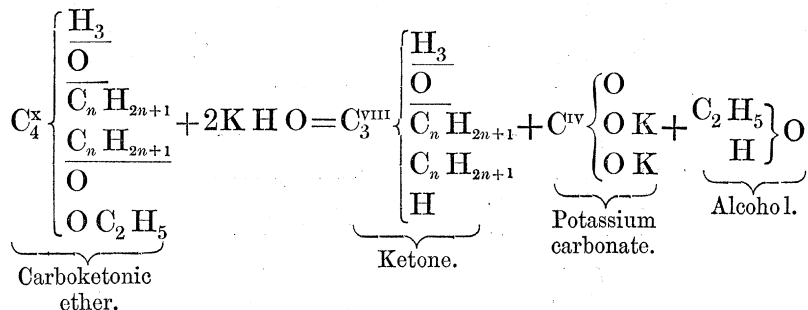
The carboketonic ether thus indicated has actually been obtained by GEUTHER according to the first of the above equations, and is described by him, in the paper above alluded to, under the name *Di-methylene-carbonic-acid-ethylene ether*. In fact he appears to have also obtained, in a free state, the acid of the above ether which is formed when the latter is placed in contact with water, although he has not yet submitted it to investigation.



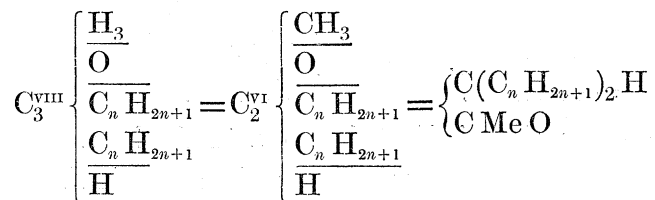
Ethylic acetone carbonate, boiled with excess of baryta-water or alcoholic potash, ought to yield, in accordance with the homologous reactions, alcohol, a carbonate of the base, and acetone, according to the following equation:—



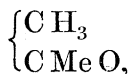
The decomposition of the carboketonic ethers by caustic alkalies is readily traced by the use of the general formulæ above given; besides alcohol, a carbonate of the alkaline metal is produced, whilst a ketone containing three atoms less of carbon than the carboketonic ether is formed.



A closer inspection of this formula for ketones shows that it does not essentially differ from that usually adopted for these bodies, since it can readily be reduced to the radical type, thus:



The composition and mode of formation of the ketones described above, together with the general methods of forming these bodies previously known, indicate the existence of many isomeric compounds belonging to this family alone, without taking into consideration the metameric bodies in the aldehyde and allyl-alcohol series. The formula of acetone,



does not allow the conception of any isomer. The formula of the next higher ketone is equally incapable of isomeric modification, for the formulæ



are only apparently isomeric. If reduced to the tetratomic carbon type, they both become  $\text{C Me Et O}$ . This is the formula of *methylated acetone*, described above, of *methylacetone* obtained by FITTIG\* in distilling lead acetate, and of *ethyl-acetyl* obtained by FREUND† in acting upon acetyl chloride with zinc-ethyl. Unless physical causes of isomerism be assumed, there can be little doubt as to the identity of these three substances, the only difference known being in their boiling-points, which are as follow:—

	Barometer.
Methylated acetone . . . . .	81° C. about 760 millims.
Ethyl-acetyl . . . . .	77°·5–78° C. about 738 millims.
Methyl acetone . . . . .	75°–77° C.

The discrepancy between the first two ceases to be remarkable when the difference of pressure at which their boiling-points were determined is taken into account, and when it is remembered that our methylated acetone probably retained traces of dimethylated acetone which boils at 93°·5 C. FITTIG does not give the boiling-point of his methyl acetone as an exact determination, remarking that “a more accurate determination of the boiling-point was obliged to be abandoned on account of the small amount of liquid available.”

The origin of FITTIG's methylacetone does not afford any satisfactory clue to its constitution, but the production of ethyl-acetyl and methylated acetone by synthetical processes, not only confirms the commonly received view of the constitution of the ketones, but also proves the identity of these two bodies. The formation of ethyl-acetyl by FREUND's process shows that it consists of two bodies of the composition of the radicals indicated by the name, whilst the formula for methylated acetone, above given, if rightly interpreted, affirms the same thing.



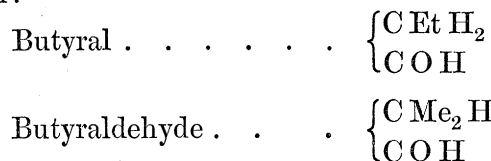
The presence of methyl in the so-called acetyl has been abundantly proved, consequently the chlorous radical is the same in both the above formulæ, whilst the formation of butyric acid, by the substitution of ethyl for hydrogen in the methyl of acetic acid, proves that ethylated methyl is identical with propyl, and that consequently methylated methyl is the same thing as ethyl, therefore the basylous radicals in the above formulæ are also identical.

Butyral, which is isomeric with methylated acetone, has been classed by KÉKULÉ amongst the ketones, but we cannot agree with this classification, as, unlike a ketone, it yields on oxidation a fatty acid containing the same number of atoms of carbon, and it also reduces with facility ammoniacal solution of silver oxide; in fact KÉKULÉ's own definition of a ketone excludes it completely from this class of bodies. Butyral does not appear to be identical with the butyraldehyde obtained by the oxidation of protein

\* Ann. der Ch. und Pharm. cx. 17.

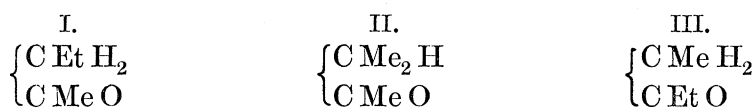
† Ibid. cxviii. 1.

bodies, for the first does not, according to CHANCEL, form a definite compound with ammonia, whilst the second does. The two following formulæ possibly express the nature of this isomerism:—



If this hypothesis be correct, the first ought to yield on oxidation normal butyric acid, and the second dimethacetic acid.

When we ascend the ketonic series one step higher, isomerism becomes possible, and the ketonic formula  $\text{C}_5 \text{H}_{10} \text{O}$  is susceptible of the three following isomeric modifications:—



At first sight it would appear that two other isomers would be produced by the introduction of propyl ( $\text{C Et H}_2$ ) and isopropyl ( $\text{C Me}_2 \text{H}$ ), thus  $\left\{ \begin{array}{l} \text{C H}_3 \\ \text{C Pr O} \end{array} \right.$  and  $\left\{ \begin{array}{l} \text{C H}_3 \\ \text{C Pr}\beta \text{ O} \end{array} \right.$ ; but a closer inspection of these formulæ shows the first to be identical with No. I. and the second with No. II. Thus, reduced to the carbonic-acid type, these formulæ become respectively



All three isomers are now known. The first of the above formulæ is that of ethylated acetone described above, which readily forms a crystalline compound with sodium bisulphite. The second is that of dimethylated acetone, which we believe to be identical with the body obtained by FITTIG\* in distilling lead acetate, and to which he gave the name ethyl acetone. Both bodies form crystalline compounds with sodium bisulphite. The boiling-point of dimethylated acetone is  $93^\circ.5 \text{ C}$ . FITTIG states that ethyl acetone boils between  $90^\circ$  and  $95^\circ$ . The only discrepancy between the two compounds is in their specific gravities, which are as follow:—

Dimethylated acetone . . . . .	·8099 at $13^\circ \text{ C}$ .
Ethyl acetone . . . . .	·842 at $19^\circ \text{ C}$ .

This discrepancy may perhaps be explained by the fact that FITTIG's ketone yielded on analysis 0·6 per cent. too much carbon, and 0·4 per cent. too little hydrogen, which would indicate that it still contained dumasine, from which it had been approximately separated by fractional distillation.

The name which FITTIG has applied to his ketone of the above composition implies that he regarded it as ethylated acetone, but the boiling-point of the latter ( $101^\circ \text{ C}$ .) precludes this supposition (see remarks about these boiling-points below).

The third of the above formulæ is that of FREUND'S† ethyl-propionyl prepared by the

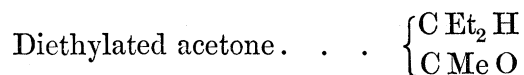
\* Ann. der Ch. und Pharm. cx. 17.

† Ibid. cxviii. 1.

action of zinc ethyl upon propionyl chloride. This body boils at  $101^{\circ}\text{C}$ . like ethylated acetone, but, unlike the latter, does not form a crystalline compound with sodium bisulphite. The origin of MORLEY'S propione\*, obtained by the distillation of barium propionate, renders its identity with ethyl-propionyl almost certain. Its boiling-point,  $100^{\circ}\text{C}$ ., is nearly the same, and, like ethyl-propionyl, it also, as FREUND has proved, refuses to form a crystalline compound with sodium bisulphite.

There are still two other compounds of this formula which have been sometimes classed as ketones, but respecting which evidence is still wanting as to whether they belong to the ketone or aldehyde family. These are LIMPRICHT and USLAR'S propione†, which boils at  $110^{\circ}\text{C}$ ., and methyl-butyral‡, which boils at  $111^{\circ}\text{C}$ . The first forms a crystalline compound with sodium bisulphite, but it is not known whether or not it reduces ammoniacal solution of silver oxide. The behaviour of the second with either of these reagents is unknown.

The seven-carbon ketones to which diethylated acetone belongs, are capable of more numerous modifications, of which however only two are known, viz.—



The isomerism of these bodies is evident from their origin, and from the difference of  $6^{\circ}$  in their boiling-points, butyrone boiling at  $144^{\circ}\text{C}$ ., whilst diethylated acetone boils at  $137^{\circ}$ – $139^{\circ}\text{C}$ . The rise in boiling-point by the successive replacement of the hydrogen of methyl by alcohol radicals affords a valuable clue to the constitution of numerous organic compounds, and attention has recently been called to this subject by KOLBE§, who has shown that the successive replacement by alcohol radicals of the three atoms of hydrogen in ammonia and in the methyl of methylic alcohol is attended with very different results

as regards elevation of boiling-point; thus the addition of  $\text{C H}_2$  to aniline  $\left( \text{N} \left\{ \begin{array}{l} \text{C}_6 \text{H}_5 \\ \text{H} \\ \text{H} \end{array} \right. \right)$

with the production of toluidine  $\left( \text{N} \left\{ \begin{array}{l} \text{C}_7 \text{H}_7 \\ \text{H} \\ \text{H} \end{array} \right. \right)$  raises the boiling-point about  $19^{\circ}\text{C}$ .; but

if the addition of  $\text{C H}_2$  to aniline converts the latter into methyl-aniline  $\left( \text{N} \left\{ \begin{array}{l} \text{C}_6 \text{H}_5 \\ \text{C H}_3 \\ \text{H} \end{array} \right. \right)$ , then

the boiling-point rises only  $10^{\circ}$ , whilst the replacement of the third atom of hydrogen appears to be attended with a rise of only about  $5^{\circ}\text{C}$ . This observation, so far as the existence of the difference described is concerned, receives considerable support from

\* Ann. der Ch. und Pharm. lxxviii. 187.

‡ Ibid. lii. 295.

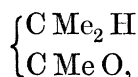
† Ibid. xciv. 327.

§ Ibid. cxxxii. 112.

the boiling-points of the ketones mentioned above, although the actual numerical expression of this difference does not coincide with that given by KOLBE. Thus acetone boils at about  $55^{\circ}\text{C.}$ , and methylated acetone at  $81^{\circ}\text{C.}$ , the difference being  $26^{\circ}\text{C.}$ ; and a comparison of the two formulæ,



shows that acetone is converted into methylated acetone by the substitution of methyl for the *first* atom of hydrogen in methyl. Dimethylated acetone,



boils at  $93^{\circ}\cdot 5$ , which is only  $12^{\circ}\cdot 5$  higher than methylated acetone. An inspection of the formula of this body shows that it is derived from methylated acetone by the substitution of methyl for the *second* atom of hydrogen in the methyl of acetone. Again, ethylated acetone is derived from acetone by the substitution of ethyl for the first atom of hydrogen in the methyl of acetone, and its boiling-point is  $101^{\circ}$  or  $23^{\circ} \times 2 = 46^{\circ}$  higher than that of acetone, whilst the boiling-point of diethylated acetone is  $138^{\circ}$  or  $18^{\circ}\cdot 5 \times 2 = 37^{\circ}$  above that of ethylated acetone. In all cases of isomerism it may be safely asserted that the body containing the fewest atoms of hydrogen replaced by an alcohol radical will boil at the highest temperature.

This is clearly seen in the following examples:—

	Name.	Formula.	Boiling-point.
Isomeric . . .	Butyral . . . . .	$\begin{Bmatrix} \text{C Et H}_2 \\ \text{C H O} \end{Bmatrix}$	$95^{\circ}\text{C.}$
	Methylated acetone . . .	$\begin{Bmatrix} \text{C Me H}_2 \\ \text{C Me O} \end{Bmatrix}$	$81^{\circ}\text{C.}$
<hr/>			
Isomeric . . .	Methyl-butyral . . . . .	$\begin{Bmatrix} \text{C Pr H}_2 \\ \text{C H O} \end{Bmatrix}$	$111^{\circ}\text{C.}$
	Ethylated acetone . . .	$\begin{Bmatrix} \text{C Et H}_2 \\ \text{C Me O} \end{Bmatrix}$	$101^{\circ}\text{C.}$
	Ethyl-propionyl . . . . .	$\begin{Bmatrix} \text{C Me H}_2 \\ \text{C Et O} \end{Bmatrix}$	$101^{\circ}\text{C.}$
	Dimethylated acetone . .	$\begin{Bmatrix} \text{C Me}_2 \text{H} \\ \text{C Me O} \end{Bmatrix}$	$93^{\circ}\cdot 5\text{C.}$

	Name.	Formula.	Boiling-point.
Isomeric . .	Butyrene . . . . .	$\left\{ \begin{array}{l} \text{C Et H}_2 \\ \text{C Pr O} \end{array} \right\}$	144° C.
	Diethylated acetone . .	$\left\{ \begin{array}{l} \text{C Et}_2 \text{H} \\ \text{C Me O} \end{array} \right\}$	138° C.

The carboketonic ethers show in a very remarkable manner the boiling-point values of different atoms of hydrogen, whilst the two isomeric bodies of this series also exemplify what has just been stated regarding the inference of constitution from the boiling-point. Reduced to the radical type, these bodies may be thus tabulated:—

	Name.	Formula.	Boiling-point.
	Ethylic acetone carbonate . . . .	$\left\{ \begin{array}{l} \text{C(C Me O)H}_2 \\ \text{C O Eto}^* \end{array} \right\}$	176° C.
	Ethylic methacetone carbonate . .	$\left\{ \begin{array}{l} \text{C(C Me O)Me H} \\ \text{C O Eto} \end{array} \right\}$	184° C.
	Ethylic dimethacetone carbonate . .	$\left\{ \begin{array}{l} \text{C(C Me O)Me}_2 \\ \text{C O Eto} \end{array} \right\}$	184° C.
	Ethylic ethacetone carbonate . . .	$\left\{ \begin{array}{l} \text{C(C Me O)Et H} \\ \text{C O Eto} \end{array} \right\}$	195° C.
	Ethylic diethacetone carbonate . .	$\left\{ \begin{array}{l} \text{C(C Me O)Et}_2 \\ \text{C O Eto} \end{array} \right\}$	211° C.

It will be seen from these formulæ that the lowest of the carboketonic ethers has already one atom of methylic hydrogen replaced by the radical acetyl (C Me O), consequently the further substitution of methyl and ethyl takes effect upon the second and third atoms of methylic hydrogen. When in the formation of ethylic methacetone carbonate the second atom of hydrogen becomes replaced by methyl, the boiling-point rises only 8° C.; but when the third atom of hydrogen is in like manner exchanged for methyl the boiling-point is not appreciably affected, ethylic methacetone carbonate and ethylic dimethacetone carbonate both boiling at the same temperature.

The introduction of ethyl in the place of the second atom of hydrogen, in passing from ethylic acetone carbonate to ethylic ethacetone carbonate, raises the boiling-point 19° C., or 9°·5 for each addition of CH<sub>2</sub>. Ethacetone carbonate contains CH<sub>2</sub> more than methacetone carbonate, and the addition is also here made to the group occupying the place of the second atom of hydrogen: in this case the addition of CH<sub>2</sub> is also attended by a rise of only 11° in the point of ebullition. Finally, the conversion of ethylic ethacetone carbonate into ethylic diethacetone carbonate, unlike the corresponding change in the methyl compounds, is attended with a marked though small rise of boiling-point equivalent to 8° C. for each CH<sub>2</sub> added.

\* Eto = Ethoxyl = (C<sub>2</sub> H<sub>5</sub> O).

Thus it is evident that the replacement of each of the three atoms of methylic hydrogen by the same alcohol radical is attended with a different result as regards the elevation of boiling-point, and that the rise in the temperature of ebullition becomes markedly less as each atom of typical hydrogen is successively replaced, although the absolute thermal values of each of the three atoms depend upon functions which have not yet been discovered.

## II. *Constitution of the Fatty Acids.*

There is perhaps no series of organic compounds which has been the subject of such numerous investigations and theoretical speculations as that of the fatty acids; nevertheless the synthesis of several of these acids, by a method of general application described in the foregoing pages, whilst confirming some previous views regarding the constitution of these bodies, has opened a path into their basylous constituent which had not previously been explored, and has disclosed the existence of vast numbers of isomers, which now require only the expenditure of time and labour for their production.

Amongst the investigations and theoretical views above alluded to, we would especially call attention to those of KOLBE and FRANKLAND\*, and of DUMAS†, which proved the existence of methyl in acetic acid, and of other alcohol radicals in the higher homologues of that acid; to FRANKLAND'S view of the constitution of the alcohol radicals themselves, a short abstract of which appeared in the British Association Reports for 1855, Trans. of Sect. p. 62‡; and of KOLBE and FRANKLAND§, who in the year 1857 proposed the derivation of these and a large number of other organic compounds from the carbonic acid or tetratomic carbon type; and finally, to a recent paper by KOLBE||, in which he predicts the discovery of dimethacetic acid, and of other similarly constituted acids.

We conceive each fatty acid to be formed by the union of a chlorous and a basylous radical. In all acids higher than the formic, these radicals are held together by one of

\* Memoirs and Proceedings of the Chemical Society, vol. iii. p. 386, and Ann. der Ch. und Pharm. lxxv. s. 288; lxix. s. 258.

† Comptes Rendus, xxv. 383.

‡ As this abstract does not appear to be generally known, we here copy it from the report in question:—

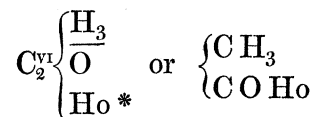
“These remarkable reactions lead the author to anticipate that zincethyl will prove in the hands of chemists a new and valuable means of research; for it is evident from its reactions that it will be capable of replacing electro-negative elements in organic or inorganic compounds by ethyl; a kind of replacement which has never yet been attempted, but which the author anticipates will enable him to build up organic compounds from inorganic ones, and ascend the homologous series of organic bodies; by replacing, for instance, the hydrogen in a methylic compound by chlorine or iodine, and then acting upon this product of substitution by zincethyl or zinemethyl, the author believes that compounds higher in the series will be obtained, since he regards the higher homologues of methyl and its compounds as derived from the latter radical by the successive replacement of hydrogen by methyl.”

§ Ann. der Ch. und Pharm. Bd. ci. s. 260.

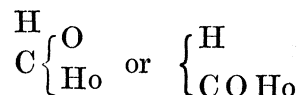
|| Zeitschrift f. Ch. u. Pharm. 1864, s. 30.



the atomicities of a carbon atom in each, as expressed in the following formulæ of acetic acid:—



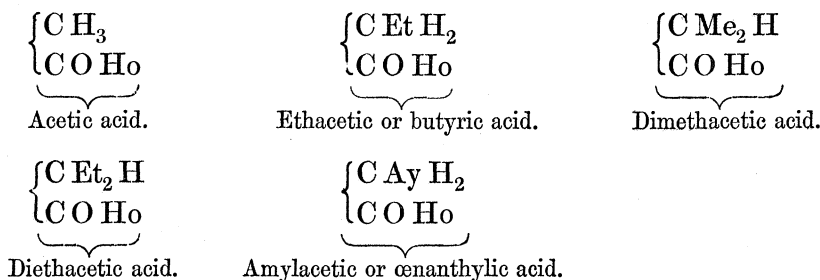
Inasmuch, however, as formic acid contains only one carbon radical, the simple basylous radical hydrogen is retained in combination with the compound chlorous radical by the fourth atomicity of the carbon atom in the latter:



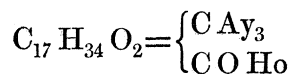
This difference in the constitution of formic acid, as compared with that of the higher members of the same family, makes itself felt in numerous well known abnormal reactions.

The chlorous radical of the fatty acids remains unchanged throughout the entire series, and it is to alterations made in the basylous radical that the separate terms of the series owe their formation.

An inspection of the above formula of acetic acid shows that its basylous radical methyl contains three single atoms of hydrogen combined with a tetratomic atom of carbon; and we have proved, by the production of the synthesized acids above described, that two of these atoms of hydrogen are replaceable by the alcohol radicals, the synthesized acids standing, with regard to acetic acid, in the relations represented by the following formulæ:—



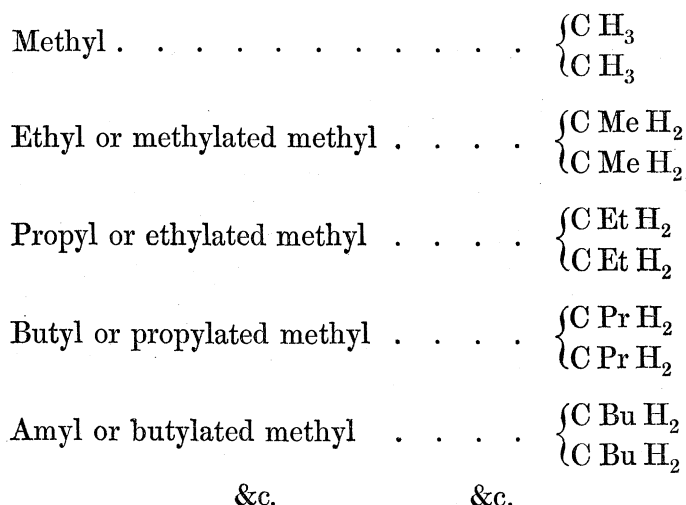
Although we have not as yet obtained with certainty acids originating from the replacement of more than two of the atoms of hydrogen in the methyl of acetic acid by alcohol radicals, yet there can be little doubt that the third atom admits of a similar substitution; and we have, in fact, obtained indications of the formation of acids depending upon this threefold replacement—an operation which, if carried out with amyl, would obviously produce triamyl-acetic acid, possessing the composition of margaric acid:



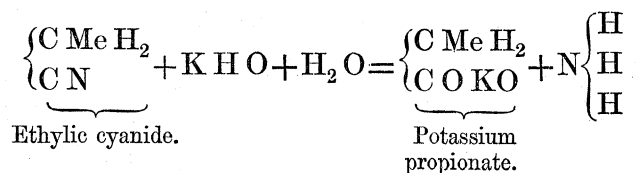
\* Ho = hydroxyl or peroxide of hydrogen = HO.

It is unnecessary at present to follow the development of this reaction further; but it is evident, from what has been already done, that by a proper selection of the three radicals put into the place of the methylic hydrogen, any fatty acid, from the margaric downwards, can be produced without difficulty.

In order to understand the relations between the synthesized and the natural fatty acids, it is necessary to remember the constitution of the latter as revealed in their production from the cyanides of the alcohol radicals; these radicals, of which the cyanides have been so employed, must consist of methyl in which not more than one atom of hydrogen has been replaced, since the alcohols containing them yield by suitable oxidation the corresponding fatty acids; whereas it has been shown by FRIEDEL\* that secondary alcohols, such as isopropylic alcohol, in which *two* atoms of methylic hydrogen have been replaced, yield, under the same conditions, ketones instead of acids. Hence the molecules of the normal alcohol radicals must possess the following constitution:—



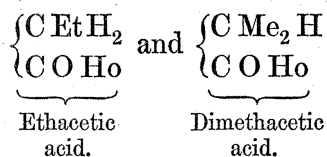
and hence when the cyanides of these radicals are boiled with caustic alkalies, they yield acids containing as their basylous constituent, the normal alcohol radicals which were present in the cyanides; thus ethylic cyanide yields potassium propionate—



An inspection of the above formula for potassium propionate shows that propionic acid is incapable of isomerism from any change of radicals; and, inasmuch as ethyl is simply methylated methyl, it follows that methacetic acid, when obtained by the substitution of one atom of hydrogen in acetic acid by one of methyl, must be identical with propionic acid, which, with acetic acid, can have no isomer depending on a difference of

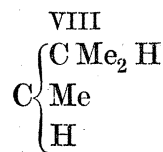
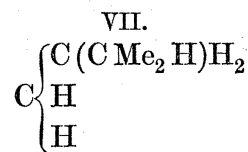
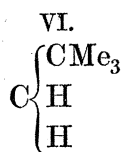
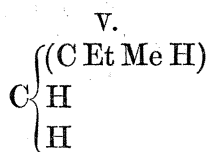
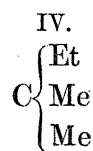
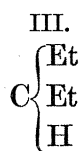
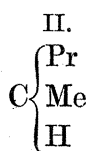
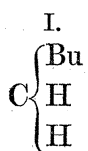
\* Bulletin de la Soc. Chimique, 1863, p. 247.

radicals. When, however, we ascend the next step of the series, we find that butyric acid is capable of two, and only two isomeric modifications, viz.,



Both these acids have now been synthetically produced, and the first must be identical with butyric acid, since they both contain ethylated methyl as their basylous radical—a conclusion which is in perfect harmony with experimented facts, for we have shown above that butyric acid and ethacetic acid are undistinguishable from each other, whilst methacetic acid differs in odour and in the crystalline form of its silver-salt.

Ascending now to caproic acid, the number of possible isomers is augmented to eight, this being in fact the number of possible metameric modifications of the basylous radical of caproic acid—amyl, viz. :—



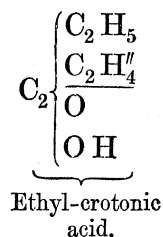
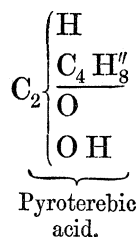
No. I. is normal amyl or butylated methyl; Nos. II., III., and IV. are obvious isomers, whilst the remainder owe their differences to the metameric modification of the radicals butyl and propyl contained in Nos. I. and II.

Of the isomeric acids, those containing the radicals Nos. I. and III. are the only ones known. The first is the caproic acid obtained by the action of potash upon amyl cyanide, and which is probably identical with the caproic acid obtained from cocoa-nut oil; whilst the second is diethacetic acid obtained as above described, and which differs from caproic acid in its odour, in the boiling-point of its ether (which is  $11^\circ \text{C.}$  lower than caproic ether), in the specific gravity of its ether, and in the crystalline form and solubility of its silver-salt.

Enanthylic acid admits of still more numerous isomeric modifications, of which only one is at present known with certainty, since, for the reasons above given, we believe amylacetic acid to be identical with the acid that would be obtained by the action of potash upon heptyl cyanide, and probably also with that obtained from castor oil and other similar sources.

Now, inasmuch as the acids obtained from the cyanides appear to be identical with the natural or non-synthesized acids of the same atomic weights, and as the alcohol

radicals in these cyanides are normal radicals, that is, methyls in which only one atom of hydrogen has been replaced, it is highly probable that all the non-synthesized acids contain normal radicals with *two* atoms of unreplaced hydrogen, just as the natural acids of the acrylic series contain, as we have proved for a large majority of them \*, the largest possible number of atoms of unreplaced hydrogen, which is one atom, thus differing from the synthesized acids of the same series which contain no unreplaced hydrogen, as seen for instance in pyroterebic acid and its synthesized isomer ethyl-crotonic acid.



This remarkable peculiarity in the constitution of the radicals of natural or analytically obtained organic compounds, must be the expression of some general law regulating the formation of those compounds, and which cannot much longer elude detection.

Intimately connected with isomerism in the fatty acids is the like phenomenon in the alcohols which has recently been remarked by KOLBE† and by FRIEDEL‡; in fact the synthesis of the carboketonic ethers and of the fatty acids lays open a direct path, through the beautiful reactions either of MENDIUS or FRIEDEL, to corresponding alcohols.

In conclusion, there can be no doubt that the reaction which forms the subject of this paper is capable of a very wide extension, and that by its means we shall be able to ascend many of the well-recognized homologous series. In future communications we hope to have the honour of laying before the Royal Society the results of its extension to the alcohols and ethers, and to the benzoic series of ethereal salts.

\* Journ. Chem. Soc. vol. xviii. p. 147.

† Zeitschrift Ch. u. Pharm. Bd. v. 687.

‡ Bulletin de la Soc. Chimique, 1863, p. 247.