

Amylic leucate is a colourless, transparent, and slightly oily liquid, possessing a fragrant odour of a somewhat amylic character. It is insoluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity is  $\cdot 93227$  at  $13^{\circ}\text{C}$ . It boils constantly at  $225^{\circ}\text{C}$ ., and its vapour has a density of  $6\cdot 74$  (theoretical  $6\cdot 97$ ).

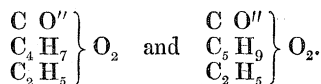
The boiling-point and specific gravity, in the liquid form, of amylic leucate and its isomer, ethylic amylethoxalate, are almost absolutely identical. Leucate of amyl is readily decomposed by either aqueous or alcoholic solutions of the alkalies, or by baryta-water, yielding amylic alcohol and a leucate of the base.

No. VII. *Action of Zinc upon a mixture of Amyl Oxalate and Amyl Iodide.*

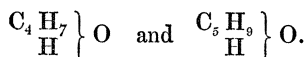
When equivalent proportions of the amyl iodide and amyl oxalate are heated gently in contact with zinc, a brisk reaction soon sets in. After evolving much hydride of amyl and amylene, the whole solidifies to a gum-like mass, which, on distillation with water, yields an oily liquid resembling that obtained when ethyl oxalate is employed. We have every reason to believe that the same series of ethers as those described in note No. V. are here produced, with the difference that they are amylic, instead of ethylic ethers. This difference of base, however, renders it impossible successfully to separate these ethers from each other, their boiling-points being so high as to determine decomposition when their distillation is attempted. We might, it is true, have decomposed the mixed ethers with solution of baryta, and thus have obtained the mixed acids, but the task of disentangling the latter appeared also so hopeless, that we have not attempted it.

IV. "Notes of Synthetical Researches on Ethers.—No. I. Synthesis of Butyric and Caproic Ethers from Acetic Ether." By EDWARD FRANKLAND, F.R.S., and B. F. DUPPA, Esq. Received April 5, 1865.

For some time past we have been engaged in the study of the consecutive action of sodium and the iodides of methyl and ethyl upon acetic ether. When iodide of methyl is used, the chief products of the reaction are two ethereal bodies possessing respectively formulæ, which we will provisionally write as follows :—

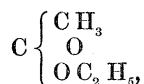


These bodies are decomposed, even in the cold, by baryta-water, yielding barium carbonate, alcohol, and two new ethereal liquids having formulæ which, without expressing any opinion as to their nature or constitution, may be thus written :—

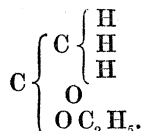


We have also obtained corresponding results by the employment of iodide of ethyl in place of iodide of methyl, and are now occupied in the preparation of a paper containing the details of this investigation, which we hope very soon to have the honour of laying before the Royal Society\*. In the meantime, however, some of our results are so remarkable that we hasten to communicate them at once in this preliminary note.

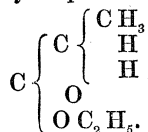
It has been proved by Kolbe and Frankland, nearly twenty years ago, that methyl is a constituent of acetic acid†, and in the year 1857 these chemists were the first to propose the derivation of this and a large number of other organic compounds from the carbonic acid or tetratomic carbon type‡. According to this view, which is now gradually receiving the assent of chemists, the rational formula of acetic ether is



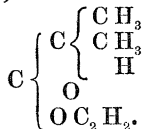
or, with the formula of the contained atom of methyl fully developed,



Thus the radical methyl, in acetic ether, contains three single atoms of hydrogen, combined with a tetratomic atom of carbon. If one of these atoms of hydrogen be replaced by methyl, an ether, having the composition of propionic ether, will obviously be produced:



If a second atom of hydrogen be replaced by another atom of methyl, butyric ether or its isomer will, in like manner, be formed:

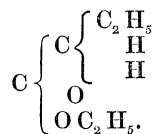


\* Whilst engaged in these experiments we became aware, through the 'Jahresbericht der Chemie,' that the reaction had already been studied by Geuther, who, however, owing to his having conducted the process in a somewhat different manner, obtained only two of the compounds above mentioned, viz. the body  $\text{C}_7 \text{H}_{12} \text{O}_3$  by the action of sodium and iodide of methyl upon acetic ether, and the compound  $\text{C}_8 \text{H}_{14} \text{O}_3$  in the corresponding reaction with iodide of ethyl.

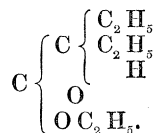
† Memoirs and Proceedings of the Chem. Soc. vol. iii. p. 386; and Ann. der Ch. und Pharm. Bd. lxv. S. 288, und Bd. lxix. S. 258.

‡ Ann. der Ch. und Pharm. Bd. ci. S. 260.

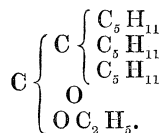
An ether, of the same composition as the last, will also obviously result, if, instead of replacing two atoms of hydrogen by two of methyl, one of those atoms be substituted by one of ethyl,



Again, if two atoms of hydrogen in the methyl of acetic ether be replaced by two of ethyl, caproic ether should result :



And, finally, if all three atoms of hydrogen be replaced by amyl, there must be produced the ether of an acid possessing the atomic weight of margaric acid :



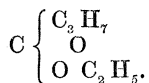
It is unnecessary to follow theoretically these reactions further ; but it is obvious, from what has been already advanced, that, by a proper selection of the three radicals put into the place of the methylic hydrogen, any ether, from the margaric downwards, can be produced at will, by a process analogous to that which we have experimentally demonstrated in the lactic series.

The present note describes the method by which we have already realized several of these substitutions.

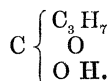
### *Synthesis of Butyric Ether.*

When sodium is gently heated with acetic ether, it gradually dissolves with evolution of hydrogen, and on cooling, the liquid solidifies to a crystalline mass, which becomes hot when mixed with iodide of ethyl, abundance of iodide of sodium being formed : nevertheless it is advisable to complete the reaction by enclosing the materials in a digester, and then heating the latter for several hours to 100° C. On distilling the crude product thus obtained with water, a large quantity of an ethereal liquid collects upon the surface of the aqueous portion of the distillate. After drying with chloride of calcium, this liquid begins to boil at about 40° C., when a considerable amount of ethylic ether comes over. Afterwards the temperature rises to 70°, between which point and 80° some acetic ether, which had escaped the action of the sodium, distils. The remainder of the distillate, which

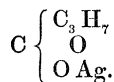
was collected apart, came over between 80° and 250°. By repeated rectification, in addition to other products, which belong to another part of the investigation, two liquids were obtained in considerable quantity, one of which boiled at 118°–122°, and the other at about 150°–157° C. On treating these liquids with boiling baryta-water for several hours, the point of ebullition of the first was rendered quite constant at 119°, and that of the second at 151°. Submitted to analysis, the first of these liquids yielded results closely coinciding with those calculated from the formula of butyric ether,



The boiling-point of the new ether also coincides exactly with that of butyric ether, as does also its vapour-density, which was found to be 3·96, the vapour-density of butyric ether being 4·04. Its density in the liquid state is ·8942 at 0° C., that of butyric ether being ·9019 at 0° C. The synthesized butyric ether is readily decomposed by alcoholic potash, yielding alcohol and a salt which, when distilled with excess of 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° C. The boiling-point of butyric acid has been variously stated by different observers: Pelouze and Gélis give it as 164°, whilst H. Kopp makes it 157°, at 760 millims. pressure. This acid gave numbers, on analysis, exactly corresponding with the formula

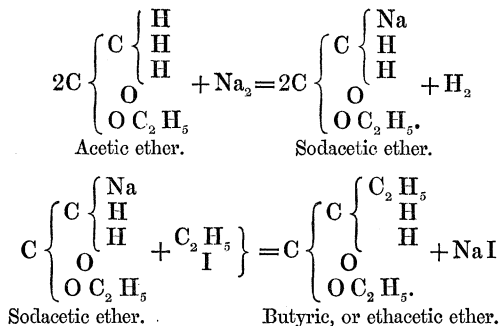


Boiled with water and silver carbonate, it yields, after some hours, a crop of beautiful ramiform needle-like crystals, aggregated into large globular masses, which become anhydrous *in vacuo*; both the mother-liquor and crystals have a faint smell of rancid butter. Submitted to analysis they yielded results closely corresponding with those required for butyrate of silver,

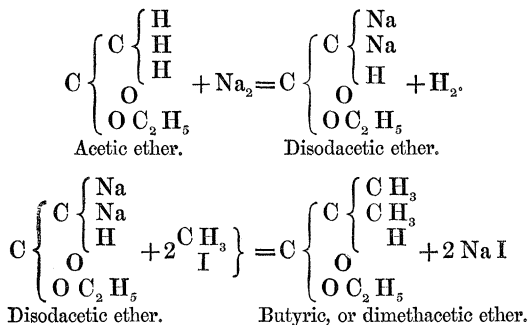


We reserve for a future communication the decision of the question as to whether the butyric acid thus obtained is identical with that produced by the process of fermentation; but we may now state that the synthesized butyric ether possesses, in a very dilute form, a fruity smell, but differing in this respect somewhat from that of the butyric ether ordinarily sold as essence of pine-apples. We have also reproduced the ether from the baryta-salt with the same result as regards odour.

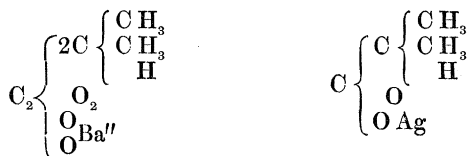
The production of butyric from acetic ether, by the consecutive action of sodium and iodide of ethyl, is expressed by the following equations:—



It has been already stated above that an acid of the same composition as butyric acid must also result from the replacement of two atoms of hydrogen, in the methyl of acetic ether, by two of methyl; and we have in fact produced this acid by first replacing the two atoms of hydrogen by sodium, and then acting upon this compound with iodide of methyl:—

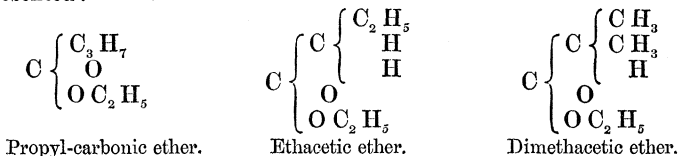


We have not yet obtained this ether in a state of perfect purity; but by acting upon the crude product of the reaction with alcoholic potash, a mixture of potassium acetate and butyrate was obtained, and yielded, by the application of Liebig's admirable method of partial saturation, butyric acid in a state of such purity that a further semisaturation produced no change in its composition. A barium salt and a silver salt made from this acid yielded results on analysis closely corresponding with the formulæ



It is thus evident that an acid, having the composition of butyric acid, can be now produced by three distinct synthetical processes, viz. 1st, by

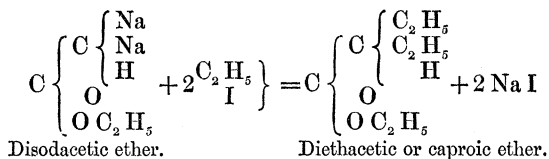
the introduction of propyl into carbonic acid; 2ndly, by the substitution of ethyl for hydrogen in acetic ether; and 3rdly, by the replacement of hydrogen by methyl in acetic ether. The ethers of these acids may be thus represented:—



Are these acids identical, or are they isomeric? We hope shortly to be able to answer this question decisively.

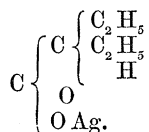
### *Synthesis of Caproic Ether.*

The production of a dimethacetic compound, as above described, obviously points out a reaction by which caproic or diethacetic ether can be obtained. It is only necessary to act upon disodacetic ether with iodide of ethyl, to obtain, with the greatest facility, the compound in question:—



Diethacetic ether boils constantly at 151° C. The boiling-point of ordinary caproic ether is stated by Lerch to be 120°, and by Fehling 162°. These numbers differ so widely that it is impossible to use them for comparison. Its specific gravity at 0° C. is .8822 (according to Fehling the density of caproic ether is .882 at 18° C.), and its vapour-density 5.00, the theoretical number being 4.98. On analysis it yielded numbers corresponding with the above formula. Diethacetic ether possesses a peculiar and somewhat pleasant odour, somewhat resembling oil of peppermint; it is insoluble in water, but miscible in all proportions with alcohol and ether. Treated with alcoholic potash it is readily decomposed, yielding alcohol and potassium diethacetate, and by distilling the latter with dilute sulphuric acid, diethacetic acid distils over and floats on the surface of the water which accompanies it. This acid reddens litmus-paper powerfully, is very sparingly soluble in water, and emits a peculiar odour, quite different from that of ordinary caproic acid. Boiled with water and carbonate of silver 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. Sub-

mitted to analysis this salt exhibited the composition required by the formula



Diethacetate of silver differs from the silver salt of the caproic acid prepared from cyanide of amyl, by its much greater solubility in water, and by its ramiform crystallization, amylic caproate of silver crystallizing in large and very thin plates, which are nearly insoluble in cold water.

In conclusion, there can be no doubt that this reaction 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. Whilst pursuing it in the acetic and benzoic series of ethereal salts, we also purpose to extend it to the alcohols and ethers.

May 4, 1865.

Major-General SABINE, President, in the Chair.

In compliance with the Statutes, the names of the Candidates recommended for election into the Society were read from the Chair, as follows :—

Henry Christy, Esq.  
The Hon. James Cockle, M.A.  
Rev. William Rutter Dawes.  
Archibald Geikie, Esq.  
George Gore, Esq.  
Robert Grant, Esq., M.A.  
George Robert Gray, Esq.  
George Harley, M.D.  
William Huggins, Esq.

Sir F. Leopold M<sup>c</sup>Clintock, Capt.  
R.N.  
Robert M<sup>c</sup>Donnell, M.D.  
William Kitchen Parker, Esq.  
Alfred Tennyson, Esq., D.C.L.  
George Henry Kendrick Thwaites,  
Esq.  
Lieut.-Col. James Thomas Walker,  
R.E.

David Livingstone, LL.D., and the Right Honourable Lord Dufferin were admitted into the Society.

The following communications were read :—

- I. "On the Properties of Liquefied Hydrochloric Acid Gas." By GEORGE GORE, Esq. Communicated by Professor STOKES, Sec. R.S. Received March 30, 1865.

In a former communication to the Royal Society "On the Properties of Liquefied Carbonic Acid," printed in the Philosophical Transactions for 1861 (also in the Journal of the Chemical Society, vol. xv., page 163)\*,

\* The reader is referred to the above communication for details of information respecting the apparatus employed and manipulation adopted.