

XLIII.—*On the Action of Sodium on Valerianate of Ethyl, viz., the Liberation of the Acid-forming Radicle Valeryl.*

By J. ALFRED WANKLYN.

MORE than twenty years ago an account of some experiments on the action of potassium upon acetic ether was published by Löwig and Weidmann.*

The result arrived at was that potassium reacts very energetically upon acetic ether, but that no gas is produced. The solid products were, moreover, found to consist partly of ethylate of potash, and partly of the potash-salt of a curious acid closely related to acetic acid, but which was only slightly examined.

This research does not appear to have attracted much attention. It was at the time unintelligible; and later, when the classical researches of Frankland and Kolbe, relating to the alcohol-radicles, came out, it seemed not to be in harmony with them. Inasmuch as metals eliminate ethyl from iodide of ethyl, it was not unnatural to suppose that they would also eliminate ethyl from acetate of ethyl and from other salts of ethyl.

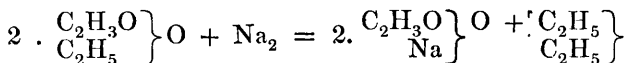
In undertaking an investigation of the action of sodium upon the ethers of the fatty acids, the first point demanding attention was whether it is really a fact that the metal does not liberate the alcohol-radicle.

I have made very careful experiments on acetate of ethyl and on valerianate of ethyl, and get results corresponding in this particular with those of Löwig and Weidmann.

I sealed up a quantity of sodium with acetate of ethyl, which had been very carefully deprived of alcohol and of water, and weighed the tube containing these materials. I then heated the tube to 130° C for some time, until the contents had

* Ann. Ch. Pharm., xxxvi, 297.

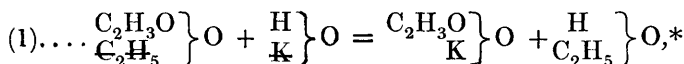
changed from liquid to solid. After opening the tube and allowing any gas that might have formed to escape, I weighed it again. The loss amounted to 0.5 in 100 parts of acetic ether. Therefore no appreciable quantity of gas is evolved in the reaction of sodium upon acetate of ethyl, and, therefore, sodium does not react upon acetate of ethyl in the manner represented by this equation—



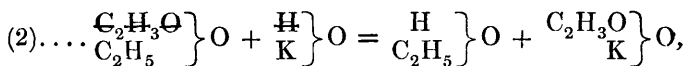
This result was confirmed in various ways. With sodium and valerianic ether, unquestionable results of a like character were also obtained.

If we consider what is really known about acetate of ethyl, we shall find that after all it is not so very clear that ethyl is the moveable portion in it.

The reaction between acetate of ethyl and caustic potash, whereby alcohol is formed, is capable of two explanations, viz. :—



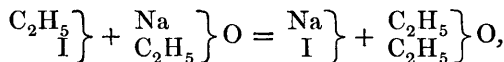
wherein ethyl and potassium change against one another.



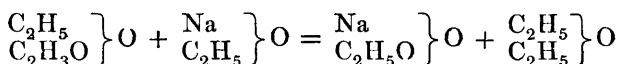
wherein acetyl and hydrogen change against one another.

The remarkable fact discovered by Beilstein, that acetic ether does not give ether by reaction with ethylate of sodium, but forms with it a double compound, which splits up, on the addition of water, into alcohol and acetate of soda, points to a fundamental want of resemblance between the ethers of the fatty acids and the haloid ethers, such as the iodides.

The well known reaction



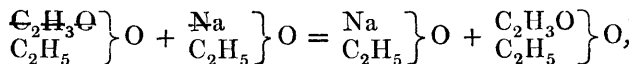
is thus seen to be without its counterpart when acetic ether is taken, the reaction



being found not to take place.

* The radicles which are supposed to replace one another are *crossed*.

If we allow that in acetic ether it is the acetyl, and not the ethyl which is moveable, then it is clear that acetic ether and ethylate of sodium cannot react so as to produce a change in the product :

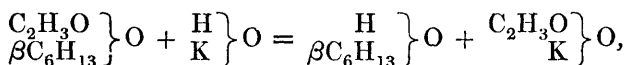


giving ethylate of sodium and acetic ether, the very compounds which were taken at first.

Many other facts which are familiar to chemists tend in the same direction ; the uniformity with which an acetate of a radicle gives the alcohol when it is treated with potash is one of them.

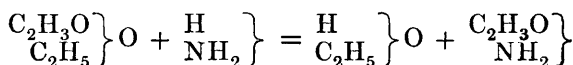
This is particularly striking in the β Hexyl series :—

Iodide of β hexyl gives hexylene with alcoholic potash. Acetate of β hexyl gives no trace of hexylene, but β hexylic alcohol instead :



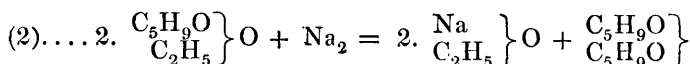
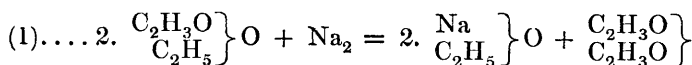
where the reaction is confined to an interchange between acetyl and hydrogen, and where, the β hexyl being undisturbed, it has little opportunity for the display of its characteristic tendency to split up into hydrogen and hexylene.

Another remarkable reaction which favours the interpretation for which I am contending, is that between ammonia—even aqueous solution of ammonia—and an ether of a fatty acid, *e.g.* :—



wherein acetic ether and ammonia give rise to alcohol and acetamide, acetyl changing against hydrogen, and not ethyl against ammonium.

After these examples of the mobility of acetyl, the following equations will not appear to be contrary to analogy :—



For obvious reasons, it is easier to investigate the action of

sodium upon valerianic ether than upon acetic ether. The advantage in dealing with a case when there is a difference in carbon-condensation between the acid-forming radicle and the alcohol-forming radicle, as in valerianic ether, over a case where, as in acetic ether, both radicles are alike in carbon-condensation, will be at once apparent.

On the present occasion, therefore, I shall give in detail an account of the examination of the action of sodium on valerianic ether, reserving the investigation of acetic ether and other ethers for a future opportunity.

The valerianic ether used in this research, after being washed and dried, boiled constantly between 132° and 135° C. A portion was digested in a sealed tube with aqueous solution of potash; it dissolved completely in the potash, leaving no oily layer.

On placing pieces of sodium in valerianic ether, the metal becomes very bright, and assumes a yellowish colour, like gold; heat is developed, but there is no evolution of gas. By and by the liquid becomes very thick, a white solid being formed, and the reaction seems to come to a stand-still on account of the extreme viscosity of the product.

In order to obtain anything like a complete reaction, it was necessary to employ some inert liquid to act as a diluent. Ether was chosen for this purpose, and before being used was washed with water, to remove any alcohol, and very completely dried, first with potash, and afterwards by distillation off fragments of metallic sodium.

The following are the details of an experiment—

2 grms. of sodium,
6 grms. of valerianic ether,
7.5 grms. of ether,

were sealed up together and heated in the water-bath. After the whole contents of the tube had become very thick—almost solid—the tube was opened, and the sodium unacted upon was cleaned and weighed. It weighed 0.7 gm. The amount of sodium which had taken part in the reaction was, therefore, 1.3 gm.

The product from which the unattacked sodium had been separated was next treated with water, when it yielded an oil and an aqueous layer which was strongly alkaline. The amount of free alkali, estimated by means of a standard solution of acid, corresponded to 1.08 gm. of sodium.

The oil, which of course contained large quantities of ether, was washed, then heated in an open vessel in the water-bath to drive off the ether, then transferred to a little bottle and weighed. After this operation it weighed 2·2 gm.

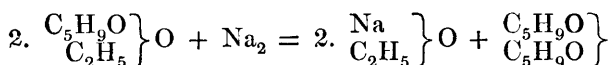
It was dried and burnt with oxide of copper, a little chlorate of potash being used.

·2680 gm. gave ·7024 gm. CO_2 and ·2815 gm. H_2O .

Carbon	71·48
Hydrogen	11·67
Oxygen	16·85
	<hr/>
	100·00

Therefore,	grms.
Valerianic ether taken	= 6
Sodium consumed	= 1·3
Sodium in caustic state	= 1·08
Oily product	= 2·2

The equation



requires :—

	grms.
Valerianic ether taken	= 6
Sodium consumed	= 1·06
Sodium in caustic state	= 1·06
Valeryl	= 3·92

It will be seen that the amount of sodium found in the caustic state is almost the theoretical quantity, and the remark may be made that the method by which this datum is arrived at is calculated to give a precise result. The sodium consumed is sufficiently near the theoretical quantity. The oil is of necessity below the mark: at least ·5 gm. would be lost by adhesion to the dish in which it was heated to drive off ether; there is a source of loss by evaporation and by solution in the water used to wash it.

On comparing the composition of the oil with the composition of valerianic ether,

Valerianic ether.	Valeryl.	Found.
C 64·62	70·59	71·48
H 10·77	10·59	11·67
O 24·61	18·82	16·85
<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

it is manifest that the oil cannot be unattacked valerianic ether; it is therefore certain that the sodium which had disappeared had used up the valerianic ether taken for the experiment.

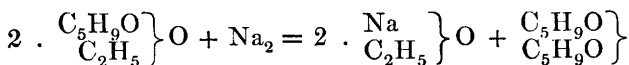
The oil approximates in composition to valeryl, the slight excess of carbon and hydrogen being probably due to the presence of a little hydrocarbon—the product of a slight secondary action of sodium upon valeryl. The circumstance that the sodium consumed is slightly in excess over the sodium found caustic, is quite in accordance with there having been a slight degree of secondary action on the valeryl.

In another experiment an oil was obtained which gave on analysis:—

Carbon	71·52
Hydrogen	11·04
Oxygen	17·44
		<hr/> 100·00

Freund* has shown that an amalgam of one part of sodium and two parts of mercury liberates a compound having the composition of butyryl from chloride of butyryl. It boils between 245° and 260°C. and appears to suffer decomposition on distillation.

Valeryl should be more readily decomposed than butyryl. I was therefore indisposed to attempt a purification of my product by means of distillation. It will be far easier so to modify the original reaction as to obtain it pure in the first instance. With this part of the investigation I am at present engaged. Meanwhile the fact that one molecule of valerianic ether is completely decomposed by one atom of sodium, and that the one atom of sodium appears in the caustic state, whilst the resulting oil has very nearly the composition of valeryl, is conclusive evidence that the reaction between sodium and valerianic ether is correctly represented by the equation



* Ann. Ch. Pharm., cxviii, 33.

With potassium the reaction is the same. One equivalent of potassium dissolves in one molecule of valerianic ether, and is subsequently found in the caustic state, whilst an oil separates just as before. In making the experiment with potassium the greatest caution is required: with care, the reaction may be effected with the greatest precision; without proper attention an explosion is the result.

From the great interest belonging to the acid-forming radicles it is my intention to prepare large quantities of valeryl, and to make a minute examination of its chemical character.

The principal other acid-forming radicles, including benzoyl, will be also sought by a similar procedure.
