XLIX.—*On the Nature of the Compound Ethers.*

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THE most convenient way of expressing the fact suggested by the action of sodium upon valerianic ether is to designate valerianic ether by the name Ethylate of Valeryl. It is thereby implied that, in the majority of reactions into which valerianic ether enters, the valeryl, and not the ethyl, is the portion which is exchangeable.

It is to be expected that this mode of reaction is very general, occurring, not only with the ethers of mono-basic, but also with those of poly-basic acids; and perhaps one of the most serviceable classifications of the compound ethers will turn out to be one

based upon this general fact, according to which they will range themselves into three classes :—

Class I. Compound ethers wherein the acid-forming radicle is usually exchangeable.

Class II. Compound ethers wherein the alcohol-forming radicle is usually exchangeable.

Class III. Compound ethers wherein acid-forming and alcohol-forming radicles are about equally exchangeable.

It will of necessity require an immense accumulation of facts before a thorough satisfactory assignment of the numerous compound ethers to these classes can be made ; but, nevertheless, it seems to me that a provisional assignment may be attempted with the employment of the data which are at present accessible.

To the first class will belong :

The ethers of the fatty acids, *i.e.*,

„ „ aromatic acids.

„ „ oxalic acid.

„ „ boracic acid.

„ „ silicic acid.

„ „ carbonic acid, &c.,

and of course many other sets of ethers which I am unable, at present, to specify.

The characteristics of these ethers of the first class are :—

(1) With alkali-metals there is replacement of the acid-forming radicle—wholly in the case of the mono-basic, and either wholly or partially in the case of the poly-basic.

(2) With organo-metallic bodies, such as zinc-ethyl, or sodium-ethyl, there is replacement of the acid-forming radicle by metal, and formation either of a ketone or else, in the case of poly-basic ethers, of a *reduced acid*.

(3) With potash (alcoholic solution) always an alcohol, never an ether.

(4) With ethylate of potassium, no reaction.

(5) With ammonia, an amide of the acid-forming radicle.

To the second class will belong :—

Iodides.

Bromides.

Chlorides.

Nitrites.

Nitrates.

Fluorides (?)

Characteristics of second class :—

- (1) With metals—alcohol-radicle, or else organo-metallic body.
- (2) With organo-metallic body—alcohol-radicle double.
- (3) With potash in alcohol—ether as well as alcohol.
- (4) With ethylate of potassium—double ether.
- (5) With ammonia—compound ammonia.

In making out the third class, it is matter for consideration whether the classification might not (with advantage) be widened, so as to include all ethers, and not merely the so-called compound ethers. If this be done, common ether and its homologues, also the double or mixed ethers, and the anhydrides, will belong to the third class.

I will now proceed to discuss some of the ethers which have been assigned to the first class. Passing over the ethers of the fatty and aromatic acids, the ethers of oxalic acid will first claim attention.

Oxalic ether, ethylate of oxalyl, is known to evolve carbonic oxide when it is heated with sodium. Carbonic oxide is the product of the splitting up of oxalyl.

Frankland and Duppa's admirable research on the action of zinc-ethyl on oxalic ether supplies the material for deciding whether that ether possesses the second characteristic.

Here follows a representation of the reaction :—

I have divided the reaction into two successive stages for the sake of clearness, and have employed a half atom of zinc ($\text{Zn}\frac{1}{2} = 32.5$).

The first equation is quite in accordance with the rule, *e.g.*, zinc replaces half of the acid-forming radicle, and produces ethylate of zinc; at the same time ethyl combines with the half-acid-forming radicle which was set free, and so a reduced mono-basic ether results.

The second equation takes place in obedience to the law

sketched out by Kekulé, viz., that an acid is in a state of stability when the number of atoms of oxygen in the acid radicle is equal to the number of atoms of hydrogen which are replaceable by metals. The acid-forming radicle $C_4H_5O_2$ not being balanced by the presence of two atoms of replaceable hydrogen, or of metal, or of alcohol-radicle, offers a point of easy attack to the zinc-ethyl, and so a case of reduction occurs as a secondary action.

Oxalic ether is well known to present characteristics 3, 4, and 5.

Respecting the relations of boracic ether, or ethylate of boron, I am likewise indebted to the researches of Frankland.

Here the acid-forming radicle boron changes against zinc, giving ethylate of zinc and methide of boron, which is exactly in accordance with the rule.

What the action of potassium or sodium on ethylate of boron is, cannot yet be stated as a fact demonstrated by experiment, but I expect it will turn out to be

In conclusion, I would again refer to Löwig and Weidmann's memoir "On the Action of Potassium and Sodium on some Salts of Ethyl," which was published in 1840.*

In this memoir the action of potassium or sodium upon formic ether, acetic ether, and benzoic ether was described. It was clearly made out that ethyl was not evolved, but that "ætherkali" was produced. So far the results obtained in 1840 seem to be correct.

The difference between the views which I have now, in 1864, to bring forward and the views of 1840 relates to the acid-forming portion of the ethers.

Precise and definite replacement of an acid-forming radicle, with occasional secondary action, is the rule to-day; in 1840 it was the old fashioned irregular reduction. But, notwithstanding the mythical nature of many of the products described by them, still

* Pogg. Ann. vii, 95, et seq.

Löwig and Weidmann were right as to the main fact, and this memoir must be pronounced to have been far in advance of its time, and to constitute one of the landmarks of organic chemistry.