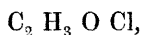


XXII.—*Researches on the Anhydrous Organic Acids,*

BY CHAS. GERHARDT.

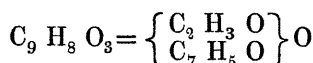
(Continuation from a Letter to Dr. WILLIAMSON.)

In continuing the researches of which I had the honour of communicating the commencement to the Society, I have found a valuable reagent not yet used in organic chemistry, and extremely valuable for the preparation of various chlorides used in the formation of anhydrous acids. This reagent is the oxychloride of phosphorus, PO Cl_3 , a liquid which effects the decomposition of a great number of salts as easily as it decomposes water, and enabled me, among other things, to prepare *Acetic chloride*,

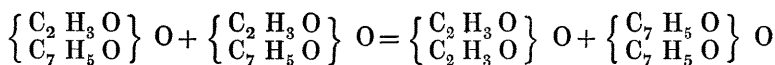


a colourless liquid, very mobile, and boiling at 56° C. It fumes slightly in the air, and is decomposed by water into acetic and hydrochloric acids. With this new chloride, I have obtained several new active compounds by double decomposition.

I prepare *acetic benzoate* or *benzoic acetate* by the action of acetic chloride on dry benzoate of soda, $C_7H_5O_2Na$. The reaction is very brisk, and is soon completed without the aid of external heat. The syrup produced, washed with water and carbonate of soda, leaves an oil heavier than water, neutral to test-paper, and possessing an agreeable odour of Spanish wine. This oil is easily purified from water and other foreign matters by agitation with ether free from alcohol; and after the ether has been removed by a gentle heat, the product shows by analysis, the composition :

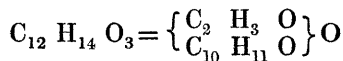


Boiling water renders it acid, but the complete decomposition requires a long action; and the intervention of alkalies is needed, as in the case of ethers. When subjected to distillation, acetic benzoate separates at about 150° into *anhydrous acetic acid* (*acetic acetate*) and *anhydrous benzoic acid* (*benzoic benzoate*). There is evidently a double decomposition between two molecules :

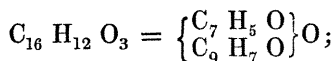


This reaction perfectly explains the formation of anhydrous acetic acid, as described in my last communication (from benzoic chloride and acetate of potassium).

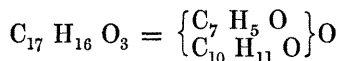
Acetic cuminate or *cuminic acetate*, is obtained in the same manner as the above anhydride. Freshly prepared, it is a fragrant oil, which preserves its liquid form in a stoppered bottle; but a few moments contact with the air is sufficient to make it crystallise, magnificent needles being formed, until the mass assumes the appearance and consistency of frozen olive oil. Analysis shews that this change of state is accompanied by no change of composition of the body :



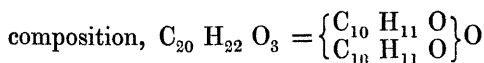
I have also succeeded in preparing in a state of purity, *benzoic cinnamate*, or *cinnamic benzoate*, a heavy, almost inodorous oil, containing



as well as the *benzoic cuminate* or *cuminic benzoate*, a similar heavy oil, containing :

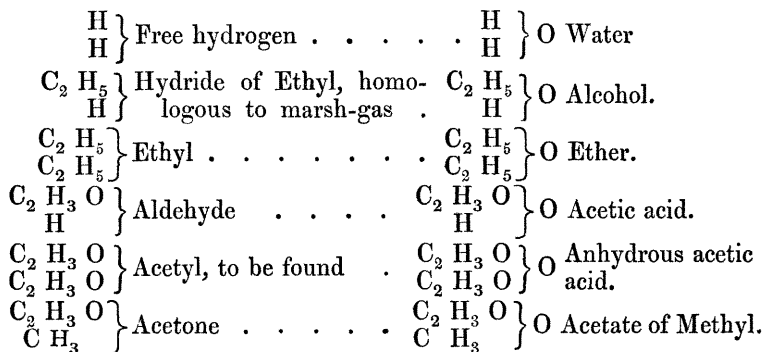


Finally also, *anhydrous cuminic acid*, or *cuminic cuminate*, is obtained by the same process, in the form of a heavy oil, resembling a fatty oil, and possessing a very faint smell. This oil also crystallises after a time ; but the oil and the crystals present the same



I am continuing these experiments with butyric, valerianic, and nitrobenzoic acids, and hope soon to be able to communicate my results to the Society.

In concluding this notice, I wish to call the attention of chemists to a remarkable analogy which exists between certain organic compounds belonging to the type water, and certain others, which I compare to the type hydrogen, as represented by the following parallel, which I submit to the consideration of experimenters.



This comparison enables me to foretel that acetyl, and in general those oxygenised groups which act like hydrogen (oxygenised radicals), will be obtained by the reaction of the corresponding chlorides on the metallic aldehydates ; and in like manner the ketones, by acting on the metallic aldehydates by the hydrochloric ethers. The experiments and considerations published on this last point by M. Chancel seem to me quite decisive.