LXV.—*The Fluorescence of Camphoric Anhydride.*

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IN a paper published some time ago (*Ber.*, **25**, 1108), I suggested a formula for camphoric acid,

which seemed at the time to be in harmony with most of the known reactions of that acid. Since then, J. Walker (this vol., p 495), in his paper on the electrolysis of sodic ethylic camphorate, has shown that in order to explain the electrolytic decomposition of sodic ethylic camphorate, and also the reactions of the dibromide of campholytic acid, camphoric acid must contain the group

If camphoric acid, therefore, is a succinic derivative, it would be a curious fact should the anhydride not give a fluoresceïn when heated with resorcin and a condensing reagent. According to Marsh (Trans., 1891, 59, 651), camphoric anhydride yields no such compound. The present communication, however, is to show that under suitable conditions a fluoresceïn can be obtained from it.

The failure of others to produce such a compound was no doubt due to the fact that unless camphoric anhydride is heated carefully with such condensing agents as sulphuric acid or zinc chloride, other reactions occur whereby the anhydride is destroyed before it has time to react with the resorcinol, sulphuric acid and camphoric anhydride giving sulphocamphylic acid, whilst zinc chloride gives tetrahydrometaxylene.

In my first attempts to prepare a fluoresceïn from camphoric anhydride, I was only able to obtain enough to give a decided green fluorescence when the product of the reaction was dissolved in alkalis. But, as a fluorescent compound was always produced whenever resorcinol and camphoric anhydride were heated in sealed tubes to a high temperature (above 300°), or when sulphuric acid or zinc chloride were used as condensing agents, I was led to try what variations in the experiment would give the largest yield of the fluoresceïn. The first series of experiments were made with strong sulphuric acid as the condensing agent. 9 grams of the anhydride were mixed with 12 grams of resorcinol and 60 grams of strong sulphuric acid. The mixture was then heated in an evaporating basin on a sand bath. There was no evolution of gas, but almost at once, on heating, the whole became a mass of white crystals. On further heating, the mixture darkened, and sulphur dioxide began to be evolved. After heating for half an hour at about 200° , the mixture had turned almost black. It was then cooled, dissolved in ammonia, the solution filtered, and acidified with hydrochloric acid. The precipitate when dissolved in alkalis gave a bright green fluorescence. This precipitate was at first thought to be the fluoresceïn, but it was soon found to be almost completely composed of a dark, brownish-black substance, which dissolved in ammonia with a splendid red colour and seemed to be allied to alizarin. It dyes cotton mordanted with alumina or ferric oxide, and is soluble in alkalis, but is reprecipitated by acids. It contains sulphur. Great difficulty was experienced in separating the true fluoresceïn from this compound, and it was only after many experiments had been tried that the following method was successful.

The precipitate which was obtained by adding hydrochloric acid to the ammoniacal solution of the products of the reaction was allowed to stand with a very dilute solution of caustic soda. By this means, only a small quantity dissolved, but most of the fluoresceïn went into

solution. After filtering, successive quantities of ferric chloride were added to the solution, whereby the precipitated ferric hydrate carried down all the colouring matter present, leaving the fluorescein still in solution. After filtering, the fluorescein was precipitated with hydrochloric acid, collected, and dissolved in a small quantity of alcohol. On the addition first of ether and subsequently of light petroleum, the pure fluorescein separated as a brown powder.

This was collected and dried. On analysis, the following results were obtained.

0.124 gave 0.326 CO_2 and 0.065 H_2O . $\text{C} = 71.67$; $\text{H} = 5.82$.

$\text{C}_{22}\text{H}_{22}\text{O}_5$ requires $\text{C} = 72.13$; $\text{H} = 6.01$ per cent.

This method is by no means a good one for the preparation of the fluorescein. The above amount, 0.124 gram, was all that was obtained from 10 grams of camphoric anhydride. It was, however, sufficient to show that camphoric anhydride gave with resorcinol a true fluorescein according to the equation

Resorcinol was treated with sulphuric acid in a precisely similar manner, but without a trace of any fluorescein being produced.

As the yield of fluorescein was so small when sulphuric acid was used as the condensing agent, the next set of experiments were made with zinc chloride. 10 grams of anhydride, 12 grams of resorcinol, and 10 grams of finely powdered zinc chloride were carefully heated in an oil bath at 180° for about an hour. The contents of the flask were then dissolved in dilute caustic soda solution, filtered, and precipitated by hydrochloric acid. The precipitate was well washed with water and then dried. In order to prepare the pure fluorescein from this crude product, the whole mass was dissolved in dry alcohol, a large excess of ether was added, and subsequently light petroleum; the precipitated fluorescein was then dissolved in soda, reprecipitated by acid, collected, and dried.

Thus prepared, camphoric fluorescein is a brown powder which does not seem to be crystalline, separating from an alcoholic solution as a powder. It dissolves in alkalis with a rose-red colour when seen by transmitted light, and shows a splendid moss-green fluorescence by reflected light.

0.0910 gave 0.2415 CO_2 and 0.0485 H_2O . $\text{C} = 72.37$; $\text{H} = 5.92$.

$\text{C}_{22}\text{H}_{22}\text{O}_5$ requires $\text{C} = 72.13$; $\text{H} = 6.01$ per cent.

When it is boiled with acetic acid and bromine, an eosin is produced, which dissolves in alcohol with a beautiful pink colour, and shows a yellow fluorescence. There, therefore, seems to be no doubt

that camphoric anhydride does give with resorcinol a true fluoresceïn compound, and the argument that it cannot be a substituted succinic acid, because its anhydride does not give a fluoresceïn, is no longer valid.

During these experiments, I have noticed that resorcinol itself, when heated with zinc chloride, yields some compound which dissolves in alkalis with a green fluorescence. This substance, however, could not be easily mistaken for a true fluoresceïn, as the fluorescence is of quite a different shade of green, a bluish-green, whilst the true fluoresceïns are a yellowish-green.

I have also heated isopropylglutaric anhydride with resorcinol and zinc chloride, and obtained unmistakable evidence that anhydrides of the glutaric series also yield fluoresceïns. The argument, therefore, that if an anhydride of a dicarboxylic acid yields with resorcinol a fluoresceïn, the substance must be an anhydride of the succinic type, is probably inaccurate.

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