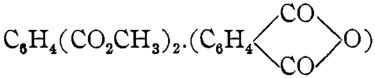
ester. If the ester were derived as suggested, its formula would be

$$[C_6H_4(CO_2CH_3)_2]_4C_6H_4(CO_2H)_2 \div 4 = C_6H_4(CO_2CH_3)_2[C_6H_4(CO_2H_2)]_{\frac{1}{4}}$$

but with the data we have at present, the only formula which can be used is



$$C_6H_4(CO_2CH_3)_2.(C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}O)_{\frac{1}{4}}.$$

It is hoped that measurement of the rate of saponification of dimethyl phthalate or of the rate of esterification of phthalic acid or of phthalic anhydride by methyl alcohol will show whether this new ester is an intermediate stage in one or more of these reactions.

Only about 0.6 g. of this ester has been prepared as the yield is very poor. This is probably due to the barium salt becoming protected by a layer of barium sulphate and it is hoped that some method of shaking the tube may increase the yield. Further investigation of this very interesting ester is in progress.

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NOTES ON CELLULOSE ESTERS.

BY R. G. WOODBRIDGE, JR.

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During the year 1907–8, the writer was engaged in the study of the chemistry of cellulose at the Massachusetts Institute of Technology, being the holder of a fellowship established for this purpose through the generosity of Mr. A. D. Little, of Boston. No limitations were placed upon the scope of the investigation except the wish of the donor that it should be of a scientific character rather than a search for results of immediate technical value. Attention was therefore mainly devoted to the study of reactions and derivatives of cellulose hitherto little known or inadequately described with the hope of throwing some light upon the chemical constitution of this important substance. As work progressed, several interesting questions presented themselves, some of which are now under investigation in the organic laboratory of the Institute. The present paper is devoted to the results of some work upon the propionates and formates of cellulose, which it is not expected to carry further at present.

Methods of Analysis.—In an investigation of this kind where it was constantly necessary to make analyses of esters prepared in various ways, the first essential was to possess a method for the determination of saponification values which should be rapid, reasonably accurate, and of such an experimental character that several determinations could be carried out at the same time.

It is well known that the method of saponification with boiling alcoholic potash, which is so useful and accurate where the esters of the simpler alcohols are concerned, does not give equally satisfactory results with the esters of cellulose. The reason seems to be that during the time necessary to split off the acyl groups, the cellulose molecule itself suffers decomposition under the influence of the alkali, and this results in the formation of acidic products. Consequently the saponification numbers obtained are high, and it was due to the use of faulty analytical methods of this kind that a tetracetate of cellulose was for some time erroneously supposed to exist.

In looking over the literature for a method which might be suitable for the purpose of the present investigation, three were found which seemed worthy of consideration.

(*a*) *The Method of Green and Perkin.*[1]—In this method, cellulose acetate is decomposed by digesting with absolute alcohol and a little concentrated sulphuric acid until half of the liquid has evaporated. More alcohol is then added and the operation repeated three times. The method seems to have given excellent results in the hands of its originators, but the writer hesitated to apply it to a large variety of products of uncertain composition because the conditions described seemed to be favorable for the formation of ethyl acetate or analogous compounds. This could only lead to a loss of acid and consequently to low saponification values.

(*b*) *The Method of Ost.*[2]—Here the cellulose acetate is dissolved in a cold mixture of one volume concentrated sulphuric acid and one of water. The solution is allowed to stand for two days and then distilled with steam. Such a distillation, continued for four hours, carries over all the acetic acid. The method seems to be accurate and reliable both according to Ost himself and the experience of the writer. It is, however, slow, and the long steam distillations involve the constant use of much cumbersome apparatus.

(*c*) *The "Sodium Ethylate" Method of Cross and Bevan.*[3]—Saponification is effected by allowing the ester to stand in the cold with a half saturated solution of sodium ethylate in a closed flask for twelve hours. This method was originally proposed for the saponification of cellulose benzoates. Its originators do not seem to have applied it to the analysis of other esters.

The writer has found that good results are obtained with a great variety of esters, both of cellulose and the lower alcohols, when the ester is allowed to stand for sixteen hours in the cold with an excess of a solution prepared by dissolving 23 grams of sodium in two liters of 95 per

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[1] *J. Chem. Soc.*, 89, 811.

[2] *Z. angew. Chem.*, 1906, I, 995.

[3] "Researches on Cellulose, 1895–1900," p. 38.

cent. alcohol. This method was finally adopted as the regular means of laboratory control in this investigation, and confidence in it has steadily increased with its use. The only precaution required is that the saponifying solution should be used in adequate excess. This is assured if about double the quantity theoretically required is employed.

In a private communication, Mr. H. S. Mork has informed the writer that it is possible to overcome the objections to the method of saponification with boiling alcoholic potash by suitable dilution of the saponifying mixture with water. He finds that in the case of an ordinary triacetate of cellulose, the suitable proportions are one volume of alcohol to one of water. Complete saponification can be effected by boiling the acetate with a half-normal solution of this character for one hour, and correct values are obtained in this way. The method has been extensively used in the laboratory of Mr. A. D. Little and has given general satisfaction.

Cellulose Propionate.—No adequate description of a cellulose propionate was found in the literature. The following experiments indicate the range of conditions suitable for the formation of the tripropionate. It can be prepared by the action of propionic anhydride upon cellulose in the presence either of sulphuric acid or of zinc chloride. The first experiments described are those with sulphuric acid.

I. Two and one-half grams filter paper were treated with a mixture composed of 15 grams propionic anhydride and 0.5 gram sulphuric acid (sp. gr. 1.84). After forty-one hours most of the cellulose had dissolved. Without attempting a separation, the mass was diluted with water and the precipitate washed and dried. The product was partially soluble in chloroform and apparently consisted of a mixture of cellulose tripropionate and unattacked cellulose. A saponification yielded 53.89 per cent. propionic acid whereas a pure tripropionate should yield 67.30 per cent.

II. Five grams filter paper were dipped in 3 per cent. sulphuric acid and after drying in the air were heated in a closed flask for three hours at 55°. According to Girard,[1] this treatment partially hydrolyzes the cellulose and renders it particularly susceptible to the action of acylating agents. The sample just mentioned, which had undergone this treatment was next allowed to stand for thirteen days in a mixture of 20 grams propionic acid and 20 grams propionic anhydride. At the end of this time the mixture was filtered and the filtrate and residue treated separately. The latter was first thoroughly washed and dried and then treated with chloroform in order to remove any tripropionate. Saponification yielded 5.9 per cent. propionic acid. It cannot be stated with certainty whether this result means that the mass contained a corresponding amount of tripropionate which the treatment with chloroform had failed to remove, or whether it indicates that some lower propionate insoluble in chloroform had been produced. In this connection it may be recalled that the mono- and diacetates of cellulose are insoluble in chloroform.

That portion of the product of acylation which was soluble in the reacting mixture after it had been filtered from the material whose properties have just been described, was precipitated with water, washed and dried. It was entirely soluble in chloroform and also in ethyl acetate. Saponification yielded 68.77 per cent. propionic acid.

III. Two grams filter paper were allowed to stand for five days with a mixture

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[1] *Ann. chim. phys.*, [5] **24**, 337, 384 (1881).

composed of 10 grams propionic acid, 10 grams propionic anhydride and 0.5 gram sulphuric acid (sp. g. 1.84). The product was entirely comparable with that obtained in II. In this case also, not quite all the cellulose was esterified.

IV. A more complete esterification can be obtained in a shorter time when zinc chloride is employed instead of sulphuric acid and the acylation is carried on at a higher temperature. For this purpose the suitable proportions seem to be about 20 grams propionic anhydride and 0.5 gram zinc chloride for each 2 g. of cellulose. When such a mixture is heated in an oil bath the cellulose begins to dissolve at about 155°. This temperature may be maintained for as long as forty minutes but should not be much exceeded. One experiment in which a temperature of 180° was maintained resulted in almost total decomposition of the product. When solution of the cellulose in the acylating mixture is nearly complete the ester may be precipitated by pouring the reaction mixture into alcohol. The product is then washed free from acid and dried at 100°.

The properties of cellulose tripropionate are essentially the same as those of the acetate. It may be distinguished qualitatively from the latter by its solubility in ethyl acetate. On spontaneous evaporation, solutions of the tripropionate yield good films but as they are no better than those which can be obtained from the acetate, and as the propionate must always remain more expensive, it is probable that this will never have any industrial importance.

Cellulose Formate.—Berl and Smith[1] have shown that cellulose monoformate may be prepared by the action of highly concentrated formic acid upon cellulose in the presence of sulphuric acid. The proportions used are 5 cc. of concentrated sulphuric acid to 100 grams anhydrous formic acid.

Experiments made in this laboratory go to show that when a formic acid of specific gravity 1.20 is substituted for the anhydrous compound, no formate is produced. On the other hand, when the strongest formic acid is employed, filter paper which has been dried at 100°, serves as well as the hydrocellulose of Girard. The conditions to be observed are well illustrated by the details of the following experiment:

Nine grams of filter paper which had been dried at 100° were treated with a mixture of 50 grams formic acid (sp. g. 1.22) and 5 grams sulphuric acid (sp. g. 1.836) for sixteen hours at a temperature ranging from 30° to 35°. The cellulose dissolved forming a thick sirup. This was "thinned" by the addition of more formic acid so that any unattacked fibers could be removed by filtration. To the filtrate water was added and the resulting precipitate was washed for a long time with water until the washings showed no acid reaction. It was then washed with alcohol and finally with ether and then dried. The product was very soluble in formic acid and also in zinc chloride solution. It was not soluble in dilute acetic, sulphuric or hydrochloric acids.[2] The formate showed a slight tendency to gelatinize in these acids but after filtration no free or combined cellulose was found in the filtrates. Cellulose formate is insoluble in the following organic solvents: methyl, ethyl and amyl alcohols, ligroin, acetone, chloroform, acetylene tetrachloride, carbon tetrachloride, ethyl acetate, amyl

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[1] *Ber.*, **40**, 907 (1908).

[2] Cf. Bemberg D. R. P. 189836, *Chem. Zentr.*, **1908**, I, 320.

acetate, aniline and nitrobenzene. Saponification yielded 23.1 per cent. formic acid. A pure monoformate should yield 24.2 per cent. Attempts made to introduce more formic acid radicles into the cellulose molecule by raising the temperature at which acylation was carried on gave only negative results. These experiments essentially go to confirm the results of Berl and Smith. Less agreement can be noted with the product described by Bemberg.[1] According to this patent it should be possible by essentially the same procedure as that outlined above to prepare a formate soluble in moderately concentrated aqueous acids. It is further stated that if cellulose be first soaked in formic acid and then pressed to a 100 per cent. gain in weight and placed in benzene containing from 3 per cent. to 10 per cent. of sulphuric acid a fibrous formate of cellulose may be obtained. It was not found possible to duplicate these results, but as the formation of a fibrous formate would have possessed considerable interest, experiments were made in which several other diluents were used instead of benzene. The latter seems particularly unsuitable for the purpose because it is not practicable to prepare a homogeneous mixture of the three liquids in the proportions suggested. Instead of benzene, experiments were made with ether, ethyl acetate, glacial acetic acid, acetone and a mixture of benzene and ether. All results were negative as far as the production of a fibrous formate was concerned. The following experiment was typical. Two grams of hydrated cellulose dried at 100° were treated with 20 grams formic acid (sp. g. 1.22), 2 grams sulphuric acid (sp. g. 1.836) and 5 grams ethyl acetate. The cellulose was unattacked and insoluble in formic acid after standing for three days. In a similar mixture which contained only 2 grams of ethyl acetate the cellulose partly dissolved but the fibrous portion was not soluble in formic acid. These experiments seem to show that the addition of even a small amount of a neutral solvent practically puts a stop to acylation, while, when the quantity of diluent is still further reduced, some acylation takes place but the product dissolves in the reacting mixture.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 169.]

RESEARCHES ON QUINAZOLINES (TWENTY-THIRD PAPER). ON 6-METHYL-7-AMINOQUINAZOLONES, 7-NITROQUINAZOLONE-6-CARBOXYLIC ACIDS, AND 1,3,7,9-NAPHTHOTETRAZINES.[2]

BY MARSTON TAYLOR BOGERT AND ALFRED H. KROPFF.

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In a recent communication[3] the authors described the preparation and properties of certain amino and nitramino derivatives of benzoic, *m*-toluic and *m*-phthalic acids of anthranilic structure, *i. e.*, with an amino group adjacent to a carboxyl, and the present paper deals with some of the quinazoline condensations obtained from these anthranilic acids. In general, these condensations depend upon the intermediate formation

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[1] *Loc. cit.*

[2] Read at the meeting of the New York Section, May 14, 1909.

[3] THIS JOURNAL, 31, 841 (1909).