Mixed chromatographs of the eluted and known DNPH's gave no separation. The spectra of the corresponding pairs of derivatives were identical, as shown in Table II.

Infrared spectra on the coniferaldehyde and the sinapaldehyde gave further evidence of their identity. A Baird double beam infrared spectrophotometer was used. The samples, dissolved in $HCCl_3$ to about 6% concentration, were run in 0.05 mm. NaCl cells, with the solvent in a matched compensating cell. The coniferaldehyde samples exhibited the same bands at 6.0, 6.2, 6.6, 6.8, 7.0, 7.3, 7.8, 8.8, 9.6 and 10.3 μ; and the sinapaldehyde samples gave the same bands at 6.0, 6.2, 6.6, 6.8, 7.0, 7.3, 7.5, 8.2, 9.6, 10.3, 11.0 and 12.2 μ. The CH bands at 3.4 and 6.8 were intensified in both wood components, and the OH band at 2.8 μ showed pronounced broadening, characteristic of hydrogen bonding.

Because of the similarities between the recovered fractions and the synthetic samples of the same compounds with relation to their chromatographic behavior, ultraviolet spectra, infrared spectra and the properties of the corresponding DNPH's, the identities of the two components of oakwood extract which give lignin-like colorations with phloroglucinol are therefore established as coniferaldehyde and sinapaldehyde.

Sinapaldehyde and Coniferaldehyde in Hardwoods and Soft Woods.—Descending paper chromatographs were run on the extracts of the different woods, as previously described for oak extracts. The developed chromatographs were examined by spraying the sheets with phloroglucinol reagent. A comparison of the sinapaldehyde and coniferaldehyde content of the woods, as indicated by the appearance of the purple colorations, is summarized in Table III.

Hibbert[17] has shown that the lignin of hardwoods is characterized by the presence of syringyl groups in addition to the guaiacyl groups of softwood lignins. In view of the structural similarities between coniferaldehyde and vanillin, on the one hand, and sinapaldehyde and syringaldehyde, on the other, it seems reasonable to conclude that sinapaldehyde is a characteristic of hardwood extractives in the same manner that syringaldehyde is a characteristic oxidation product of hardwood lignins. In general, this idea has been borne out by the chromatographic comparison of several hardwoods and softwoods. The softwoods clearly contained coniferaldehyde, while the hardwoods showed the presence of sinapaldehyde as well as coniferaldehyde. Only two woods in the group examined failed to show evidence of extractable phloroglucinol-reacting aldehydes. Apparently some woods do not contain these aldehydes in a free state. To evaluate the degree of correlation, more species of both hardwoods and softwoods will have to be examined.

TABLE III

	Coniferaldehyde	Sinapaldehyde
Post oak (*Quercus stellata*)	+	+
Forked leaf oak (*Quercus alba*)	+	+
White maple (*Acer saccharum*)	+	+
Butternut (*Juglans cinera*)	+	+
Black walnut (*Juglans nigra*)	+	+
Avodiré	+	+
Philippine mahogany	+	+
Black cherry (*Prunus serotina*)	Nil	Nil
Yellow pine (*Pinus sp.*)	+	Nil
Douglas fir (*Pseudosuga taxifolia*)	+	Nil
Cypress (*Taxodium distichum*)	+	Nil
Redwood (*Sequoia sp.*)	Nil	Nil

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[17] H. Hibbert and M. J. Hunter, THIS JOURNAL, **61**, 2190 (1939); H. Hibbert, J. J. Pyle and L. Brickman, *ibid.*, **61**, 2198 (1939); H. Hibbert, J. L. McCarthy and R. H. S. Creighton, *ibid.*, **63**, 3049 (1941).

[CONTRIBUTION NO. 325 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

Rapid Acetylation of Impregnated Cellulose*

BY JOHN C. THOMAS

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Soluble, high-molecular-weight cellulose triacetates have been prepared in extremely short reaction times by the action of acetic anhydride, at temperatures above 90°, on cellulose impregnated with certain combinations of compounds from aqueous solution and dried. For example, cotton linters impregnated with 38% of their weight of urea and 2% of their weight of ammonium sulfate reacted with excess acetic anhydride in one minute at 138° to give a soluble triacetate with a DP (degree of polymerization) of 585. In the same system at 95°, acetylation was complete after 13 minutes, and a product with a DP of 720 was formed. Other compounds could be used in place of urea and ammonium sulfate. The presence of both types of impregnants was necessary, and structural requirements for active impregnants of each type were determined.

Although there is a large amount of published work, especially in the patent literature, on the use of various types of compounds for treating cellulose to make it more active toward esterification, one technique for achieving such activation has apparently received little attention. This is the impregnation of cellulose with an activating agent from aqueous solution, followed by drying. Haller and Ruperti[1] found that cellulose impregnated in this way with the potassium salt of a weak acid, *e.g.*, potassium acetate, was active toward acetylation with acetic anhydride. Marschall[2] used for this purpose the ammonium salt of a strong acid, *e.g.*, ammonium sulfate or ammonium perchlorate. The present paper describes a new method of activation and esterification, which involves impregnating cellulose with certain *combinations* of compounds and esterifying with acid anhydrides at elevated temperatures.

It was shown in this Laboratory, in confirmation of the work of Haller and Ruperti, that cellulose impregnated from aqueous solution with 40% of its weight of potassium acetate could be acetylated beyond the diacetate stage with excess boiling acetic anhydride. The cellulose retained its original form and had the same DP (degree of polymerization) as the starting material (*ca.* 1850), but the reaction was slow, requiring about 20 hours, and the product was insoluble in organic liquids. It also was found that cellulose impregnated with 40% ammonium sulfate could be completely acetylated under the same conditions in 30 minutes. However, the product, although soluble in organic solvents, was degraded to a DP of about 50.

In searching for an activating agent that would have the advantages of both potassium acetate and

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* Presented before the Division of Cellulose Chemistry at The A.C.S. Meeting in Chicago, Ill., September 9, 1953.

[1] R. Haller and A. Ruperti, U. S. Patent 1,930,895 (1933).

[2] A. Marschall, U. S. Patent 2,172,447 (1939).

ammonium sulfate, combinations of compounds were tried. Certain combinations of two different types of impregnants imparted to cellulose a high activity toward acetic anhydride at temperatures above 90°, which activity was not realized with either impregnant alone. Thus, cotton linters impregnated from aqueous solution with, for example, a mixture of urea:ammonia sulfate in the ratio of 38:2%, based on the weight of the cellulose, reacted vigorously with excess boiling acetic anhydride at 138° to give a clear solution in one minute. From this solution there could be precipitated a cellulose triacetate having a DP of 585. (Commercial yarn-grade cellulose acetate has a DP of about 350.) The product was soluble in glacial acetic acid and in methylene chloride and insoluble in acetone. DP's as high as 760 were realized at lower temperatures.

The two types of impregnants required in combination for this method of acetylation were a "swelling impregnant" (*e.g.*, urea), present in 10–40% concentration (based on cellulose), and a "catalyst impregnant" (*e.g.*, ammonium sulfate), in 1–10% concentration.

Active swelling impregnants included carboxylic amides, carboxylic acid salts of ammonia and primary and secondary amines, polyalcohols, a polyether and water. Carboxylic acid salts of tertiary amines and quaternary ammonium hydroxides were inactive. A practical limit on active swelling impregnants was that they had to be capable of forming at least 10–20% solutions in water, so that impregnating solutions could be made up.

Active catalyst impregnants included oxy-acids of sulfur, their half amides and esters, and salts of all these acids with ammonia and primary and secondary amines. Salts of these acids with tertiary amines and quaternary ammonium hydroxides, ammonium and amine salts of organic sulfonic acids, and ammonium salts of all other inorganic acids tested were inactive. It is noteworthy that salts of relatively weak and unstable acids like ammonium tetrathionate and diethylamine sulfite had the same "catalytic" activity as ammonium sulfate.

A list of combinations of impregnants that promoted rapid acetylation is given in Table I. Pairs of impregnants that did not bring about rapid acetylation are listed in Table II.

On the basis of a combination of short reaction time and high molecular weight of cellulose acetate produced, urea was the best swelling impregnant, and ammonium sulfate was as good as any catalyst impregnant. Impregnation of cotton linters with urea and ammonium sulfate and acetylation of the impregnated cellulose with excess boiling acetic anhydride was used as a standard procedure, upon which a study of reaction variables was based.

TABLE I

ACTIVE COMBINATIONS OF IMPREGNANTS

Urea: sulfuric acid
- ammonium sulfate
- ammonium bisulfate
- hydrazine sulfate
- aniline sulfate
- diethylamine sulfate
- piperidine sulfate
- morpholine sulfate
- sulfamic acid
- ammonium sulfamate
- diethylamine sulfamate
- morpholine sulfamate
- ammonium methyl sulfate
- ammonium *n*-dodecyl sulfate
- ammonium persulfate
- ammonium sulfite
- diethylamine sulfite
- ammonium thiosulfate
- ammonium tetrathionate

N,N′-Dimethylurea: ammonium sulfate
Acetamide: sulfuric acid
Acetamide: ammonium sulfate
Hydroxyacetamide: ammonium sulfate
Ammonium formate: ammonium sulfate
- acetate: ammonium sulfate
- acetate: hydroxylamine sulfate
- ethylenediamine sulfate
- hydroxyacetate: ammonium sulfate
- adipate: ammonium sulfate
- salicylate: ammonium sulfate
- thiocyanate: ammonium sulfate

Methylamine acetate: methylamine sulfate
Aniline acetate: aniline sulfate
Hexamethylenediamine adipate: ammonium sulfate
Diethylamine acetate: ammonium sulfate
Diethylamine acetate: diethylamine sulfate
Piperidine acetate: piperidine sulfate
Morpholine acetate: morpholine sulfate
Dimethylamine dimethyldithiocarbamate: ammonium sulfate
Water: ammonium sulfate
Glycerol: ammonium sulfate
Diethylene glycol: ammonium sulfate
Diethylene glycol diethyl ether: ammonium sulfate

Experimental

Materials.—Buckeye cotton linters (DP *ca.* 1850) and Rayonier "Rayaceta" wood pulp (DP *ca.* 1200) were used. They were obtained from the Acetate Division, Textile Fibers Department, E. I. du Pont de Nemours & Co., Waynesboro, Va. Mallinckrodt A. R. 95% acetic anhydride (1.0 g. $(CH_3CO)_2O$/ml.) and Mallinckrodt A. R. 99.5% acetic acid were used. All other compounds were at least "pure" grade or were purified by distillation or crystallization.

Analytical Methods.—Values of Ac/G.U. (acetyl groups per glucose unit) were calculated from saponification numbers, which were determined by saponification with potassium hydroxide in excess ethanol at room temperature. Combined sulfur was determined as SO_4 by oxidation with Eschka mixture (sodium carbonate and magnesium oxide) and precipitation of sulfate as barium sulfate. DP's of acetic acid-soluble cellulose acetates were calculated from the following form of Staudinger's equation

$$DP = 4780 \log_{10} \eta_r$$

where η_r is the relative viscosity of a solution of 0.1 g. of cellulose acetate in 100 ml. of glacial acetic acid at 25°.

DP's of cellulose acetates (and celluloses) insoluble in acetic acid were determined from viscosities in cuprammonium solution. A graph relating viscosity of cuprammonium solution to DP of cellulose in the solution (determined in this laboratory from ultracentrifuge data) was used. Solutions for viscosity determinations were made by dissolving a weight of cellulose acetate corresponding to 0.25 g. of

TABLE II

INACTIVE COMBINATIONS OF IMPREGNANTS

Triethylamine acetate:triethylamine sulfate
    ammonium sulfate
Urea:triethylamine sulfate
Urea:triethylamine sulfamate
Pyridine acetate:pyridine sulfate[a]
Urea:pyridine sulfate[a]
Benzyltrimethylammonium acetate:benzyltrimethylammonium sulfate
Benzyltrimethylammonium acetate:ammonium sulfate
Urea:benzyltrimethylammonium sulfate
Triethylmethylammonium formate:ammonium sulfate
Ammonium acetate:ammonium sulfanilate[a]
    p-toluenesulfonate
    aminomethanetrisulfonate
    methanetrisulfonate[a]
    bromide
    chloride
    nitrate
    monohydrogen phosphate
Ammonium bisulfite:ammonium sulfate[a]
    dihydrogen phosphate
Ammonium hypophosphite:ammonium sulfate
Urea:ammonium arsenate
    borate
    chromate
    dichromate
    nitrate
    dihydrogen phosphate
    monohydrogen phosphate
    hypophosphite
    selenate
    thiocyanate
    trifluoroacetate
Urea:sulfamide[a]
    aluminum sulfate[a]
    cadmium sulfate[a]
    cobalt sulfate
    copper sulfate[a]
    ferrous sulfate
    manganese sulfate
    magnesium sulfate
    nickel sulfate
    potassium sulfate
    sodium sulfate
    zinc sulfate[a]
    sodium sulfite
    sodium thiosulfate
    zinc chloride

[a] Although these impregnants did not promote rapid reactions like that described under "Acetylation at 138°"; *i.e.*, reactions characterized by sudden disintegration of the cellulose and vigorous ebullition, they did give slower reactions, characterized by gradual disintegration of the cellulose, leading to soluble cellulose triacetates.

cellulose in 10 ml. ACS of standard cuprammonium[3] solution, and viscosities were determined at 25°.

Acetylation at 138° ("Standard" Procedure).[4]—Ten and four-tenths grams of cotton linters containing 4% moisture was allowed to stand for 30 minutes at room temperature in an aqueous solution containing 38% urea and 2% ammonium sulfate. The linters were centrifuged to a wet weight of 20 g. and dried in a vacuum desiccator over anhydrous calcium chloride at room temperature. The dried impregnated linters weighed 14 g. and were assumed to contain 38% urea and 2% ammonium sulfate, based on the dry weight of cellulose. They were added to 300 ml. of boiling acetic anhydride at 138° in a 500-ml. round-bottom flask with a wide mouth. A condenser was immediately attached to the flask, and the mixture was heated with constant manual swirling. The reaction proceeded as follows:

Time (min.:sec.)	Remarks
0:00	Linters added
0:30	Linters swollen; slight ebullition
0:45	Linters disintegrating rapidly; vigorous ebullition
0:55	Very vigorous ebullition
1:00	Slightly cloudy solution
1:05	Essentially clear, colorless solution; no ebullition
1:30	Same, but very slight color. Product was pptd. by pouring mixture into aq. 10% acetic acid

To precipitate the product, the hot solution was poured into two liters of aqueous 10% acetic acid at 65° with vigorous agitation by a "Lightnin'" mixer. A white, flocculent solid precipitated immediately. The solid was agitated for 15 minutes in the precipitation medium, filtered, washed thoroughly with distilled water and dried in a draft oven at 65°. There was obtained 17.5 g. (quantitative yield) of white, fluffy cellulose triacetate containing 2.97 Ac/G.U. and 0.03% combined sulfate and having a DP of 585. The product was soluble in hot glacial acetic acid and did not precipitate when the solution was cooled. It was soluble in methylene chloride and insoluble in acetone.

Acetylation at 95°.—Ten and four-tenths grams of cotton linters was impregnated with urea:ammonium sulfate (38:2) as described above. The dried, impregnated cellulose was added to 300 ml. of acetic anhydride at room temperature in a 500-ml. round-bottom flask with a wide mouth. Heating on a steam-bath was begun, and the mixture was stirred mechanically under a reflux condenser. The reaction proceeded as shown

Time (min.:sec.)	Remarks
0:00	Stirring and heating started
4:00	Temperature *ca.* 95°
15:00	Linters swollen; no other change
16:00	Linters disintegrating
16:30	Jelly-like mixture
17:00	Smooth, slightly cloudy, very slightly colored soln.
18:00	Same. Product was pptd. by pouring mixture into aq. 10% acetic acid

The product was precipitated and worked up as described above. There was obtained 17 g. of white, fluffy cellulose triacetate containing 2.91 Ac/G.U. and 0.08% combined sulfate and having a DP of 720. The product had the same solubilities as the one made at 138°.

Effects of Changes in Reaction Variables in the Procedure for Acetylation at 138°

Addition *vs.* Impregnation of Activating Agents.—Much slower reactions took place when both activating agents were simply added to the anhydride with the cellulose instead of being impregnated in the cellulose, or when either compound was impregnated and the other was added.

Impregnation from a Non-aqueous Solvent.—Cotton linters impregnated with acetamide:sulfuric acid (39:1.5) from glacial acetic acid and dried had not reacted completely with boiling acetic anhydride after one hour. Linters impregnated with the same combination from aqueous solution underwent rapid acetylation with boiling acetic anhydride.

Temperature.—Lowering the temperature from 138° to 95° increased the required reaction time and gave products of higher DP. The highest DP's realized in this work (up to 760) were obtained by this method. Below 90°, under a variety of conditions, acetylation either was incomplete or did not take place at all.

Concentrations of Impregnants.—Decreasing the concentration of urea in the cellulose from 38% increased the required reaction time and decreased the DP of the product.

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[3] E. K. Carver, et al., *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).

[4] J. C. Thomas, U. S. Patent 2,585,516, 1952.

Two per cent. ammonium sulfate gave the product of highest DP at 138°. Increasing the concentration above 2% did not affect the reaction time and lowered the DP. Decreasing the concentration below 2% increased the time and also lowered the DP. At 95°, 1% ammonium sulfate gave the highest DP. Increasing and decreasing the concentration had the same effects as at 138°.

Structures of Swelling Impregnants.—On the basis of a combination of short reaction time and high DP of product, urea was superior to all other swelling impregnants tested. This was true in spite of the induction period that was always observed in acetylations involving urea, but never with acetamide or the acetates of ammonia or primary or secondary amines. Thus, although acetylation times as low as 15–30 seconds were realized with the acetates and sulfates of some primary and secondary amines at high catalyst concentrations, the products were of lower DP than those of longer reactions involving urea:ammonium sulfates. Reactions with urea and a secondary amine sulfate (*e.g.*, urea:morpholine sulfate (36:4)) started later, because of the induction period, than reactions with the secondary amine acetate and secondary amine sulfate at the same concentration (morpholine acetate: morpholine sulfate (36:4)), but once under way were extremely rapid, usually finished sooner, and gave products of higher DP. The induction period with urea was longer at 95° than at 138°. Ammonium acetate was equivalent to acetamide at 138° but gave slower reactions at 95°. Both gave slower reactions than urea and the acetates of primary and secondary amines. N,N′-Dimethylurea was less active than urea. Glycerol, diethylene glycol and diethylene glycol diethyl ether were slightly less active than urea.

Structures of Catalyst Impregnants.—At equal molar concentrations, the activities of sulfuric acid and its salts with ammonia and primary and secondary amines were the same. The corresponding derivatives of sulfamic acid had the same or slightly lower activities. The two ammonium alkyl sulfates tested were less active than ammonium sulfate. Ammonium sulfite was as active as ammonium sulfate, but ammonium thiosulfate was less active. Ammonium persulfate and ammonium tetrathionate gave faster reactions but products of lower DP.

Amount or Concentration of Anhydride.—Simply lowering the amount of acetic anhydride increased the required reaction time and decreased the DP of the product. Replacing part of the anhydride with an inert solvent or non-solvent for cellulose triacetate usually had the same effect (see following). No experiments with higher amounts of anhydride were conducted.

Structure of Anhydride.—Propionic anhydride reacted with impregnated linters at its boiling point (170°) and at 95° to give cellulose tripropionates. The reaction was slower than with acetic anhydride under the same conditions (95°), and the products were of lower DP. *n*-Butyric anhydride was less reactive at 95° than propionic anhydride; the highest degree of substitution attained was about 2.6 butyryl groups per glucose unit. Chloroacetic, methoxyacetic, trimethylacetic, succinic, maleic and phthalic anhydrides gave only very low degrees of substitution. Mixtures of acetic anhydride and succinic, maleic or phthalic anhydride gave cellulose acetates containing none of the other acyl groups.

Type of Cellulose.—Wood pulp had the same reactivity as cotton linters. Viscose rayon staple and cuprammonium rayon staple were less reactive.

Acetylations in Solvents for Cellulose Triacetate.—Replacing part of the acetic anhydride with an inert solvent for cellulose triacetate, and thereby lowering the anhydride: cellulose weight ratio from 30:1 to 4–8:1, increased the required time and almost always gave a product of lower DP. Complete acetylation took place in dioxane, β,β′-dichlorodiethyl ether, nitromethane, ethylene carbonate, glacial acetic acid and diethyl sulfate. Only with dioxane were high DP (500–640) products obtained. Acetic acid and diethyl sulfate had strong degrading effects. Most of the reactions were conducted at reflux temperatures; the variation in boiling points was doubtless the cause of some of the differences in reaction times. Partial acetylation took place in trioxane, triacetin, benzaldehyde, chloral and ethylene dibromide. No visible reaction beyond swelling was observed in dimethylformamide, acetamide, dimethylacetamide, acetylmorpholine, cyclohexanone, acetonylacetone or epichlorohydrin. No reaction took place in three chlorinated solvents boiling below 95°—methylene chloride, chloroform and ethylene dichloride.

Acetylations in Non-solvents for Cellulose Triacetate (Heterogeneous Acetylation).—Acetylation of impregnated linters also could be carried out by a "heterogeneous" process, in which part of the acetic anhydride was replaced by a non-solvent for cellulose triacetate. This method had the advantage that the fibrous form of the linters was preserved throughout, and the precipitation step was eliminated. Otherwise, the experimental procedure was the same as with acetic anhydride alone. The reaction was stopped by removal of the fibrous material when a small sample of same as found to be soluble in glacial acetic acid. The product was freed from traces of the acetylation liquid by pressing on a suction filter and washing with ethanol prior to washing with water and drying. Non-solvents used were mixed xylenes, toluene, 2,2,3-trimethylpentane and diethylene glycol diethyl ether. Reaction temperatures were 95–134°.

Replacing part of the anhydride by inert non-solvents in this manner increased the required reaction time and gave products of lower DP, as in acetylations in solvents for cellulose triacetate. The highest DP, 655, was attained in 50 minutes in 2,2,3-trimethylpentane at 97° with an 8:1 anhydride:cellulose ratio. Acetylation proceeded faster in 2,2,3-trimethylpentane than in diethylene glycol diethyl ether at the same temperature (95°). Reactions in benzene at 89–93° were incomplete. Analyses of samples removed during the course of acetylation showed the existence of the induction period with urea, previously observed in acetylations with acetic anhydride alone. The effects of changes in temperature, concentrations of impregnants and anhydride, and structure of impregnants were the same as in acetylation with acetic anhydride alone.

Discussion

The mechanism by which a combination of impregnants such as urea and ammonium sulfate brings about this rapid acetylation of cellulose has not been determined. However, a few tentative conclusions can be drawn from the experimental results at hand.

Function of the Catalyst Impregnant.—The sharp falling off of the activity of ammonium sulfate below 90° suggests that ammonium sulfate itself is not the actual catalyst, but that it undergoes a reaction with acetic anhydride to give a product that is the catalyst, and that this reaction does not take place to any appreciable extent below 90°. A corresponding reaction apparently can take place between acetic anhydride and the ammonium salts of other sulfoxy acids (except organic sulfonic acids in which there is a carbon–sulfur bond), but not with the salts of other acids. Since the salts of primary and secondary amines are also active but those of tertiary amines and quaternary ammonium hydroxides are not, it appears that acetylation of the amine portion of the salt may be involved in the formation of the actual catalyst.

Function of the Swelling Impregnant.—There is little doubt that active swelling impregnants containing nitrogen are acetylated in the course of rapid acetylation of cellulose. The isolation of monoacetylurea from one reaction mixture corroborates this view.[5] The main question is whether acetylation of such an impregnant is an essential step in the process of acetylating the cellulose or whether the function of the impregnant is simply to maintain the swollen, active state of the cellulose following evaporation of the water, its acetylation being merely a parallel, not an essential, reaction.

The following facts support the thesis that ace-

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[5] P. W. Morgan, private communication.

tylation of the swelling impregnant is an essential step: (1) The acetylation at 95° of cellulose impregnated with urea:ammonium sulfate follows the same course as the acetylation of urea in the presence of ammonium sulfate or sulfuric acid at about 100°; *i.e.*, there is an induction period of several minutes and then a sudden, vigorous reaction.[6] A sample of cellulose removed from the mixture after 14 minutes in the procedure for acetylation at 95° (near the end of the induction period, before the rapid change in appearance) was found to contain only 0.27 Ac/G.U., or 9% of the triacetate acetyl content. (2) Salts of tertiary amines, which cannot be acetylated, are inactive swelling impregnants.

The following points can be made for the thesis that acetylation of the swelling impregnant is not an essential step: (1) Diethylene glycol diethyl ether, which contains no free hydroxyl groups, is an active swelling impregnant. To see whether diethylene glycol diethyl ether would be degradatively acetylated under the conditions used in acetylation of cellulose, diethylene glycol diethyl ether, ammonium sulfate and excess acetic anhydride were heated together at 138° for five minutes. No ethyl acetate was isolated, and the amount of saponifiable material (not identified) distilling with unchanged ether at the boiling point of ethylene glycol diacetate corresponded to a 4% yield of this ester. (2) The apparent inactivity of carboxylic acid salts of tertiary amines and quaternary ammonium hydroxides as swelling impregnants may actually be due to the real inactivity of the corresponding sulfates as catalyst inpregnants. Thus, when the water in a solution containing 38% triethylamine acetate and only 2% ammonium sulfate is evaporated from cellulose, most of the sulfate may be left behind as triethylamine sulfate (an inactive catalyst impregnant). A corresponding metathesis might take place in a 38:2 benzyltrimethylammonium acetate:ammonium sulfate mixture.

Acknowledgment.—I am indebted to Dr. M. L. Ernsberger for many helpful discussions and suggestions in connection with this work.

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(6) R. C. Blume, private communication; see also E. A. Werner, *J. Chem. Soc.*, 1120 (1916).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Selective Hydroxyl Reactivity in Methyl α-D-Glucopyranoside[1]

BY M. L. WOLFROM AND M. A. EL-TARABOULSI[2]

RECEIVED JUNE 10, 1953

Following the general technique of Gaver, methyl monosodio-α-D-glucopyranoside was prepared. On methylation, this produced the 2-methyl ether, characterized as the crystalline triacetate. Benzylation gave a sirup in which the presence of an open glycol group was demonstrated by periodate cleavage. Xanthation of the monosodium derivative was not possible without the addition of small amounts of water but thereupon yielded the 2-(methyl xanthate), characterized as the crystalline triacetate. Although these reactions proceeded in low yield, it is believed that they are best interpreted as indicating that, in the main, the sodium formed a true alkoxide at position two of the glucoside which then reacted by replacement to yield derivatives substituted in this position.

The question of a possible selective reactivity of the hydroxyl groups of the D-glucopyranoside structure is of interest both from the synthetic and theoretical points of view. The enhanced reactivity of the 2-hydroxyl function as compared to that of other secondary hydroxyl groups, in carbohydrates, has been noted primarily in reactions requiring alkaline media. This effect is probably a result of the greater acidity of the hydrogen on the hydroxyl group adjacent to a carbonyl or to a potential carbonyl group. The preparation of 2-O-methyl-D-glucose diethyl thioacetal (mercaptal) by Lieser and Leckzyck[3] and of 2-O-methyl-starch by Gaver[4] constitute examples of the selective reactivity of the 2-hydroxyl in reactions requiring alkaline media.[5] Alkali and alkaline earth hydroxides appear to form "addition complexes" with sugars and polysaccharides.[6,7] These have been scrutinized by Percival and collaborators[8] to determine at what points the base was bound. They concluded that the various sugars behave rather differently but show a common feature in that positions 2 and 6 are especially capable of reaction. These addition compounds are unstable and while they are much utilized in the cellulose field, this instability is undesirable.[9] Gaver,[4] however, in his studies on the action of alkali on starch in non-aqueous media, was able to prepare a monosodium "starchate" which had a true alkoxide structure and in which the sodium had largely replaced the hydrogen of the 2-hydroxyl. Following Gaver's work, Sugihara and Wolfrom[10] prepared a monosodiocellulosate in which the sodium was mainly on the second position of each anhydro-D-glucose unit. The purpose of the present investigation was to extend Gaver's monoalkala-

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(1) Presented before the XIIIth International Congress of Pure and Applied Chemistry, Stockholm, Sweden, August 1, 1953.

(2) Fellow of the Egyptian Government.

(3) T. Lieser and E. Leckzyck, *Ann.*, **511**, 137 (1934).

(4) K. M. Gaver, Dissertation, The Ohio State University, 1945; U. S. Patents 2,397,732 (1946), 2,518,135 (1950), 2,609,368 (1952); *Abstracts Papers XIIth Intern. Congr. Pure and Appl. Chem.*, 623 (1951); K. M. Gaver, Esther P. Lasure and D. V. Tieszen, U. S. Patent 2,572,923 (1951); K. M. Gaver, Esther P. Lasure and L. M. Thomas, U. S. Patents 2,602,084 and 2,609,367 (1952).

(5) For a review on the selective reactivities of the hydroxyl groups in carbohydrates, see J. M. Sugihara, *Advances in Carbohydrate Chem.*, **8**, in press.

(6) J. Groot, *Biochem. Z.*, **180**, 341 (1927).

(7) J. E. Mackenzie and P. J. Quin, *J. Chem. Soc.*, 951 (1929).

(8) W. J. Heddle and E. G. V. Percival, *ibid.*, 1690 (1938); E. G. V. Percival, *ibid.*, 1160 (1934); 648 (1935); E. G. V. Percival and G. G. Ritchie, *ibid.*, 1765 (1936).

(9) Z. H. Skraup and R. Kremann, *Monatsh.*, **22**, 1037 (1901).

(10) J. M. Sugihara and M. L. Wolfrom, THIS JOURNAL, **71**, 3509 (1949).