dines resulting from the action of ammonia on aldehydes likewise lose hydrogen and pass into the corresponding pyridines.[13] The hydrogen resulting from the conversion of III into IV above always fell considerably below the amount theoretically expected. Perhaps some of this hydrogen was utilized in forming reduction products, and some of the dihydro bases (III) may have been polymerized to a tar, without loss of hydrogen.

β- and γ-substituted pyridines and quinolines were not isolated in the present work, although it is posible that they are formed in small quantity. The migration of the alkyl or aryl group of formula I from nitrogen to the 2-carbon then does not strictly follow the migration of an alkyl group from nitrogen to the 2 and 4 carbons in the Ladenburg synthesis of alkyl pyridines and quinolines.[14]

Summary

1. Pyridine, quinoline and isoquinoline react with the Grignard reagent in diethyl ether solution at 150–160° to form α-alkyl or aryl pyridines, quinolines or isoquinolines in yields varying between 44 and 66% of the theoretical.

2. The following compounds have been prepared: 2-ethylpyridine, 2-phenylpyridine, 2-phenylquinoline and 1-ethylisoquinoline. 1-Ethylisoquinoline has been prepared for the first time.

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[CONTRIBUTION FROM THE LABORATORIUM FUER CHEMISCHE TECHNOLOGIE DER UNIVERSITAET WIEN, VIENNA, AUSTRIA, AND NORTHWESTERN UNIVERSITY, MEDICAL SCHOOL, DEPARTMENT OF RESEARCH BACTERIOLOGY, CHICAGO, ILLINOIS]

CELLULOSE SULFONIC ACID ESTER

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In a preliminary report[1] the formation of a trisulfonic acid ester derived from cellulose was reported. This compound was obtained by the action of chlorosulfonic acid in an excess of pyridine on cellulose (pure filter paper or cotton). Data were given as to its formation, general properties and analysis.[2] It was found that films and threads can be formed from this ester and its salts.

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[13] Chichibabin, *J. prakt. Chem.*, **107**, [N. F.] 122 (1924).

[14] Ladenburg, *Ber.*, **32**, 42 (1899); **16**, 1410, 2059 (1883).

[1] Gebauer-Fuelnegg, Stevens and Dingler, *ibid.*, **61**, 2000 (1928).

[2] In the first report the statement has been made that a second treatment of cellulose-trisulfonic acid ester with the pyridine chlorosulfonic acid reagent will give a purer substance and complete the triesterification. We were unable to repeat the results of the respective preliminary experiments, from which the figures have been taken. On the contrary, it was found that under certain circumstances one SO_3H group is eliminated by this procedure. We will report on this reaction later.

It was pointed out that the pyridine salt of the ester did not show rotation in aqueous solution, nor did it reduce Fehling's solution, and contrasted in these properties appreciably with a cellulose sulfonic acid ester prepared recently by Traube and co-workers.[3] These authors prepared the ester by the action of sulfur trioxide on well-dried cotton. There are, however, certain similarities between the two cellulose sulfonic acid esters.

The ester obtained by Traube and co-workers is stated to be a derivative of undegraded cellulose. As to the structure of the ester obtained by the action of the pyridine-chlorosulfonic acid reagent on cellulose, however, we have considered three possibilities. (I) The product might be a derivative of undegraded cellulose, an assumption supported by the fact that no rotation or reduction of Fehling's solution could be observed. (II) The ester might be a degradation product of cellulose. (III) It might be a degradation product of cellulose which on further action of the pyridine-chlorosulfonic acid reagent repolymerized to form a cellulose-like carbohydrate.

In the first paper it was stated that even though equality in fundamental properties such as reducing power and rotation would be expected if both products were derived from undegraded cellulose, the differences actually observed could be ascribed to the different preparational methods, according to ideas recently developed by Kurt H. Meyer and H. Mark.[4]

To determine whether or not our ester is a derivative of undegraded cellulose, hydrolysis of the sulfonic group was attempted with various agents. It was found that the trisulfonic acid ester mentioned showed the same resistance to splitting of the ester group as did the ester described by Traube. In fact, the latter author failed to find a suitable method for hydrolysis of his preparation.

A large variety of hydrolyzing agents was tried, such as ammonia, alkalies of various concentrations, alkyl amines and water, but no appreciable effect was noticed. Even dilute acids did not change the compound materially; concentrated hydrochloric acid only was found to split off the SO_3H groups, but intense degradation was observed with this reaction, as would be expected. Finally, methyl alcoholic hydrochloric acid (0.25–1%) was found to be a suitable hydrolyzing agent at 100–120°. In the course of the work it was found that boiling with methyl alcohol containing 5% of hydrogen chloride gas for a few hours also effected the hydrolysis.

The product obtained was a sulfur and nitrogen (pyridine) free white powder soluble only in cellulose solvents such as ammoniacal copper oxide, from which it could be precipitated without chemical changes.

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[3] Traube and co-workers, *Ber.*, **61**, 754 (1928).

[4] Meyer and Mark, *ibid.*, **61**, 610 (1928).

A small methoxyl content was detected, apparently due to the methylating action of the methyl alcoholic hydrochloric acid.

The rotation values of the ammoniacal copper oxide solutions showed the presence of chemically unchanged (but hydrated) cellulose and were comparable with parallel tests made with native cellulose.

Even though the results of this hydrolysis clearly showed that the sulfonic acid ester obtained by the pyridine-chlorosulfonic acid reagent was a true derivative of cellulose, an attempt was made to convert the product of hydrolysis, by acetylation and methylation, into definite cellulose derivatives of known properties. A direct exchange of the sulfonic groups of the original ester with methyl or acetyl groups also was attempted.

Acetylation and methylation of the hydrolysis product were found to be successful, while the direct exchange of the SO_3H groups of the original ester did not yield definite compounds.

The product of acetylation was triacetylcellulose, the rotatory power of which was found to be the same as that given for the triacetyl derivative of native cellulose.

Methylation also was finally accomplished, but some difficulties were encountered. There are methods for permethylation of cellulose described by Irvine,[5] Hess and Pichelmayer[6] and Urban and Freudenberg.[7] In order to find the most suitable method for the product in question, preliminary experiments were carried out with regenerated cellulose of other (known) origin, but with some relation as to the preparational method and general appearance of the substance in question. Hydrolysis of triacetylcellulose prepared with acetic anhydride and sulfuric acid, it was thought, would give such a related cellulose upon hydrolysis, since the cellulose regenerated is reported to be insoluble in alkali as is the cellulose regenerated from the trisulfonic acid ester. Accordingly this was used in the preliminary work.

The methylation method of Hess and Pichelmayer therefore at first was thought not to be suitable since it is used with alkali-soluble cellulose. The method of Urban and Freudenberg also was found to be unsatisfactory for this purpose. Even on increasing the amount of reagent and repeating the procedure, products of low methoxy content were obtained. Finally, the procedure given by Hess and Pichelmayer actually was used with good results. After nine successive methylations a trimethylcellulose with 43% methoxyl was obtained.

As expected, this method was found to be suitable for the methylation of the cellulose regenerated from the trisulfonic acid ester; the trimethyl-

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[5] Irvine, *J. Chem. Soc.*, **123**, 529 (1923).

[6] Hess and Pichelmayer, *Ann.*, **450**, 31 (1926).

[7] Urban and Freudenberg, *Cellulosechemie*, **7**, 73 (1926).

cellulose obtained was found to be identical with the trimethylcellulose described by Hess and co-workers. It might be added that the solubility in water of the trimethylcellulose from cellulosetrisulfonate is practically negligible. It is known that trimethylcelluloses are increasingly soluble in water with increasing degree of depolymerization, derivatives of native cellulose being less soluble than preparations from slightly degraded cellulose. This fact is a further indication that the cellulose trisulfonic acid ester is a derivative of comparatively slightly degraded hydrated cellulose.

Experimental Part

Attempts to Hydrolyze the Pyridine Salt of the Cellulose Trisulfonate.—The pyridine salt of the cellulose trisulfonate is prepared by adding 3 g. of carefully dried cotton to a mixture of 11.6 g. of chlorosulfonic acid and 27.4 g. of pyridine (care!) and heating the reaction mixture on the water-bath for one hour. Swelling of the cellulose is noticed first and a sirupy, viscous mass is finally obtained. The mixture is cooled and water is added, from which the ester salt is precipitated, for example, with alcohol. This is repeated several times. Details of procedure and constitution of the reagent are given in the earlier report.[1]

(a) No hydrolysis could be effected on shaking the pyridine salt with an excess of water for three days, nor by boiling under reflux for eight days.

(b) With $N/50$, $N/10$, $N/2$ and 2 N potassium hydroxide no hydrolysis of the SO_3H groups could be effected, either on the shaking machine or on boiling under reflux.

(c) Aqueous hydrochloric acid of various higher concentrations was found to effect the splitting of the SO_3H groups on boiling, but its use resulted in a degradation of the cellulose part of the substance.

(d) Finally the hydrolysis was accomplished with methyl alcoholic hydrochloric acid. The best results for this type of hydrolysis of the above salt were obtained by heating a sample with absolute methyl alcohol containing 0.25% of dry hydrogen chloride gas in an autoclave at 110°. A dark, clear, pyridine-containing liquid and a white powder were obtained. The liquid gave a sulfate reaction and a strong reduction of Fehling's solution; a small amount of an osazone could be precipitated, indicating the presence of sugars. The residue was washed with water (negative test for sulfate). A determination of the methoxyl groups gave the following results: subs., 6.475 mg.: AgI, 0.799 mg. Found: OCH_3, 1.63.

This product was white, contained no nitrogen or sulfur, was insoluble in water but was soluble, however, in hot 2 N potassium hydroxide and in cuprammine solution. It was possible to dye it with substantive dyes in the same shade and fastness as cotton.

(e) The most convenient method of hydrolyzing the SO_3H groups was the following: 50 g. of ester salt was boiled under reflux for six hours with 200 cc. of methyl alcohol to which 5% of concd. aqueous hydrochloric acid was added. After filtration of the brownish-yellow pyridine sulfate-containing liquid, the residue was extracted in a Soxhlet apparatus with boiling water until no sulfate could be detected. It was then washed with alcohol and ether. Only a very small portion of the product thus obtained was found to be soluble in hot strong potassium hydroxide and precipitable from it with acids. After drying it at 100° the product was found to have lost its solubility in alkalies. It is, however, easily soluble in cuprammine solution. The specific rotation was determined with the light of so-called "Effektkohlen" for blue light.

Hydrolyzed product (1.2991 g.) was placed in a 100-cc. volumetric flask, mixed with 1.3522 g. of copper hydroxide prepared according to the method of J. Habermann,[8]

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[8] Habermann, *Z. anorg. Chem.*, 50, 318 (1906).

wetted with concd. ammonia and diluted to the mark of the flask. A slight turbidity could not be removed either by filtration or by centrifuging the solution. In order to obtain comparable results a parallel run was made with native cellulose (cotton). The product of hydrolysis showed: $\alpha = 7.50°$; cotton, $\alpha = 6.75°$; methoxyl content of product of hydrolysis, traces only.

Acetylation of the Product of Hydrolysis.—In parallel runs 20 g. each of the above product of hydrolysis (prepared according to Procedure (e)) and cotton was heated at 30° for eight hours with 75 cc. of glacial acetic acid, 75 cc. of acetic anhydride and 2 cc. of concd. sulfuric acid. Since the product of the above hydrolysis was not entirely dissolved, both mixtures were treated for sixteen hours more. They were filtered through a glass filter. The solution obtained from the native cotton was found to be more viscous than the product obtained from the regenerated cellulose. The acetylcellulose was separated in the ordinary way by precipitation in water, filtration, drying in a desiccator and purification by dissolving in chloroform and precipitating with ether.

The yields of crude products were 90% obtained from cotton and 81% from regenerated cellulose.

$$\text{Triacetate from cotton } \left[\alpha\right]_{D}^{16} = \frac{100 \times 0.64°}{2 \times 1.4780} = -21.65° \ (\text{CHCl}_3)$$

$$\text{Triacetate from regenerated cellulose } \left[\alpha\right]_{D}^{16} = \frac{100 \times 0.54°}{2 \times 1.2431} = -21.72° \ (\text{Chloroform})$$

Both triacetates were hydrolyzed according to the procedure given by Hess[9] with methyl alcoholic sodium hydroxide and found to yield identical products, as expected.

Methylation.—Ten grams each of the above products of hydrolysis (from native cellulose-triacetate and from the triacetate obtained from hydrolyzed cellulose trisulfonate) were powdered and treated for several days with 20 cc. of potassium hydroxide (1:1); 80 cc. of water was added and methylation was accomplished with dimethyl sulfate according to the method of Hess and Pichelmayer.[8] The reaction was carried out at 55–60° in nine successive steps. The dimethyl sulfate was added drop by drop, with efficient stirring, as indicated in Table I.

TABLE I

PREPARATIONAL DATA

Steps	H_2O, cc.	NaOH, g.	$(CH_3)_2SO_4$, cc.	Minutes	Steps	H_2O, cc.	NaOH, g.	$(CH_3)_2SO_4$, cc.	Minutes
I	100	10	5	10	IV	..	50	..	10
II	...	15	.	10		..	..	10	10
	...	..	5	10		..	..	10	10
	...	..	5	10		..	..	..	30
	...	..	.	30	V	100	100	40	180
III	...	20	.	10	VI	75	125	20	180
	...	..	5	10	VII	25	50	10	180
	...	..	5	10	VIII	25	50	10	180
	...	..	.	30	IX	25	50	10	180

The first isolation of the reaction product was accomplished after the fifth step, by washing the mixture on a hot-water funnel with boiling water until freed from sulfate. For the next methylation the residue was transferred to the reaction flask with the proper amount of ice water. After the seventh step the product obtained was slightly soluble in benzene. The ninth methylation yielded a substance almost entirely soluble in benzene. Purification was accomplished by repeatedly dissolving the product

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[9] Kurt Hess, "Chemie der Cellulose und ihrer Begleiter," page 415.

in benzene and precipitating it with ligroin. The fractional extraction with ice water as given by Hess and Pichelmayer was found to be superfluous since the products in both cases were found to be insoluble. After the reprecipitation the product was treated with ether and finally dried in a vacuum to constant weight. The analyses prove the presence of a trimethylated product.

Anal. Subs., 4.552 mg.: CO_2, 8.734 mg.; H_2O, 3.211. Subs., 4.309 mg.: AgI, 13.794 mg. Subs., 0.1177: CO_2, 0.2278; H_2O, 0.0840. Subs., 0.1528: AgI, 0.5177. Calcd. for $C_6H_7O_5(CH_3)_3$: C, 52.91; H, 7.90; OCH_3, 45.50. Found: (on crude product before reprecipitation) C, 52.34; H, 7.89; OCH_3, 42.29; (pure product) C, 52.80; H, 7.99; OCH_3, 44.77.

The rotation of the trimethylcellulose obtained by the hydrolysis of cellulose trisulfonate was

$$\left[\alpha\right]_{D}^{21} = \frac{100 \times 0.18^\circ}{1 \times 0.9751} = -18.46^\circ \text{ (benzene)}$$

The rotation of trimethylcellulose obtained by the hydrolysis of triacetylcellulose was

$$\left[\alpha\right]_{D}^{21} = \frac{100 \times 0.21^\circ}{1 \times 1.1302} = -18.58^\circ \text{ (benzene)}$$

Summary

To determine whether a trisulfonic acid ester obtained from cellulose by the action of a pyridine-chlorosulfonic acid reagent on cellulose was (1) a derivative of undegraded or very slightly degraded cellulose, (2) a degradation product or (3) a repolymerized degradation product, it was hydrolyzed by means of methyl alcoholic hydrochloric acid. The sulfur-free product of hydrolysis showed (in cuprammine solution) a rotation of the order of magnitude given for native cellulose. Even though this was already a fairly good proof that the original ester was a true derivative of cellulose, this product of hydrolysis was converted to trimethyl- and triacetylcellulose. The products obtained were found to be most closely related to known preparations from native cellulose. The direct conversion of the cellulose trisulfonic acid ester into trimethyl- or triacetylcellulose could not be accomplished.

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