Spiropentane (I). In a 5-l. three-necked creased flask fitted with a high-speed stirrer, a solids-addition apparatus, and a water-cooled reflux condenser in series with a spiral condenser (arranged for distillation) and two Dry Ice traps, was placed 852 g. (2.57 moles) of disodium dihydrogen ethylene diaminetetraacetate, 297 g. (7.43 moles) of sodium hydroxide dissolved in 510 ml. of water, 1470 ml. of 95% ethanol, and 20.7 g. (0.138 mole) of sodium iodide. The mixture was heated to reflux, and 214.5 g. (3.28 g.-atoms) of zinc dust was then added. A slow stream of nitrogen was passed through the system to carry volatile products to the cold traps, and 321 g. (0.828 mole) of pentaerythrityl tetrabromide was added slowly to the stirred, refluxing mixture. After the addition was complete, the mixture was stirred at reflux temperature for 1 hr. The condensate in the cold traps was washed with two 150-ml. portions of a cold, saturated solution of sodium chloride in water and then dried over Drierite to give 45.5 g. (81%) of crude spiropentane.

Vapor chromatography (Perkin-Elmer Model 154B; column B, di-2-ethylhexyl sebacate as stationary phase) of a sample of crude spiropentane showed five other components to be present besides spiropentane. Collection of three of these in pure form by vapor chromatography of a sample of crude hydrocarbon, which had been enriched in the low-boiling impurities by fractional distillation, and comparison of their infrared spectra with those of known compounds permitted identification of 2-methyl-1-butene,[8] 1,1-dimethylcyclopropane,[9] and ethanol. Methylenecyclobutane was identified by comparison of its retention time on the column with that of a known sample. The major component was identified as spiropentane by comparison of the infrared spectrum of the crude hydrocarbon with the published spectrum.[9] The crude hydrocarbon from one run was found to be 94% spiropentane, 4.2% 2-methyl-1-butene, 0.7% 1,1-dimethylcyclopropane, 0.6% methylenecyclobutane, 0.2% ethanol, and 0.3% of an unidentified low-boiling material (possibly neopentane).

Spiropentane was obtained free of unsaturated impurities by rough titration of a 20% (by volume) solution of the hydrocarbon in ethylene dibromide with bromine, followed by distillation through a 4.5-ft. spiral-wire column. The product (b.p. 36.5–37.5°) had an infrared spectrum in agreement with the published spectrum[9] of spiropentane.

Acetylacetone was tried as a sequestering agent also and was found to be less satisfactory than ethylenediaminetetraacetate. When the theoretical amounts of acetylacetone and sodium carbonate were used to chelate the zinc ion generated in the reaction, a 60% yield of hydrocarbon containing 76% spiropentane (by base-line infrared analysis) was obtained. Smaller amounts of acetylacetone and sodium carbonate gave much smaller yields of spiropentane.

Methylenecyclobutane (II) in pure form for infrared and vapor chromatographic analysis was prepared by the method of Roberts and Sauer.[2] The reaction of 6 g. of zinc bromide, 18 ml. of ethanol, 700 ml. of water, 225.6 g. of zinc, and 406.8 g. of pentaerythrityl tetrabromide gave methylenecyclobutane in 19% yield. The product, b.p. 40.5°, was purified by distillation through a 4-ft. spinning-band column, and its infrared spectrum agreed with the published spectrum.[2]

Acknowledgment. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We would also like to thank Mr. James Brader and his associates for the infrared spectra.

URBANA, ILL.

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[8] American Petroleum Institute, Research Project 44 at National Bureau of Standards, *Infrared Absorption Spectrograms, Vol. I*, No. 196.

[9] F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Chlorination of Cellulose with Thionyl Chloride in a Pyridine Medium

ROBERT L. BOEHM

Received January 10, 1958

Activated cotton linters were treated with thionyl chloride in anhydrous pyridine to form cellulose derivatives containing up to 1.3 stable chlorine atoms per anhydroglucose unit. Unstable sulfur groupings, presumably in the form of sulfurous acid esters, were also introduced. Chlorocelluloses were hydrolyzed in aqueous sulfuric acid solution without loss of chlorine, but resistance to hydrolysis was encountered as the degree of chlorine substitution was increased. A hydrolyzate was fractionated chromatographically; glucose was isolated from one fraction and a monochloroglucose from another.

The chemical literature contains very little information concerning the halogen derivatives of cellulose. Past investigations revealed that halogens had been introduced into cellulose during the preparation of the tosyl and mesyl esters,[1] but the presence of halogens was generally considered to be of only secondary importance. The tosylation of carbohydrates in general and accompanying chlorination has been extensively reviewed by Tipson.[2] Pacsu and Schwenker[3] have recently prepared 6-mesyl chloro, 6-mesyl bromo, and 6-mesyl iodocelluloses by partial replacement of the 6-mesyl group by the appropriate halogen.

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[1] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933); F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939); A. L. Bernoulli and H. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940); M. L. Wolfrom, J. C. Sowden, and E. A. Metcalfe, *J. Am. Chem. Soc.*, **63**, 1688 (1941); J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942); C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **70**, 2740 (1948); E. Heuser, M. Heath, and W. H. Shockley, *J. Am. Chem. Soc.*, **72**, 670 (1950); R. Roberts, *J. Am. Chem. Soc.*, **79**, 1175 (1957).

[2] R. S. Tipson, *Advances in Carbohydrate Chemistry*, Academic Press, New York, Volume 8, p. 107.

[3] E. Pacsu and R. F. Schwenker, Jr., *Textile Research J.*, **27**, 173 (1957)

Carré and Mauclère[4] studied the reaction of cotton linters with thionyl chloride in a pyridine medium and obtained a substance with the formula ($C_6H_9O_4Cl$). The cotton was darkened during the course of the reaction and suffered a loss in tenacity. A more detailed investigation is given in this paper.

EXPERIMENTAL

Cotton linters. A commercially purified grade[5] contained 98.5% alpha-cellulose, 0.06% ash, had a solubility of 4.1% in hot sodium hydroxide solution, and a degree of polymerization of 1200. It was treated in a laboratory Wiley mill and screened; the fraction which passed through a 100-mesh screen and was retained on a 325-mesh screen was collected.

The linters were activated with 18% sodium hydroxide (25 ml. per gram of linters) for 4 hr. at 24–26°, washed on a tared coarse fritted-glass crucible with absolute methanol until the washings were no longer alkaline to phenolphthalein, and then five successive times with anhydrous pyridine (distilled over barium oxide). Care was taken to prevent drying of the cellulose on the filter. The quantity of activated linters available for the chlorination reaction was calculated from the yield of mercerized linters.

Thionyl chloride. Practical-grade thionyl chloride was purified by three distillations over sulfur and acetone, quinoline, and linseed oil.[6] The purity (100%) was ascertained[7] by allowing samples to distill quantitatively into a known excess of sodium hydroxide solution overnight at room temperature, and back-titrating with hydrochloric acid to phenolphthalein endpoint.

Chlorination of cellulose. Anhydrous pyridine and thionyl chloride (50.0 and 10.0 moles per mole of anhydroglucose unit, respectively) were added to the activated pyridine-moist linters, with cooling, if necessary. Reaction solutions at room temperature were shaken mechanically; those at elevated temperatures were agitated in a water bath with a mercury-sealed stirrer.

The products were then suspended in water and aqueous sodium hydroxide gradually introduced to 0.15*N* strength. After standing overnight, the suspensions were neutralized with dilute sulfuric acid; the products were washed with water until the filtrates were colorless and then air-dried.

Acidic chlorite treatment. The crude chlorocelluloses were purified by a wood pulp chloriting technique.[8] Samples (6–7.5 g.) were suspended in 300 ml. of water, acidified with 0.75 ml. of glacial acetic acid, treated with 3.0 g. of sodium chlorite, heated at 70–80° for 0.5 hr., filtered, and washed with water until free of chloride ion. In two cases (B and C) the treatment was repeated twice.

Preparation of chlorocelluloses with high sulfur content. Terminating the chlorination reaction by adding the reaction mixture slowly to cold water, filtering after 1 hr., soaking overnight in half-saturated sodium bicarbonate solution, and washing until the filtrates were colorless, gave a sample (D) with a higher sulfur content.

Pouring another chlorination mixture into absolute methanol, filtering after 1 hr., soaking in methanol overnight, and then extracting the product in a Soxhlet apparatus (*in vacuo* at 30–40°) gave a sample (E) with a still higher sulfur content.

Chemical analyses. All samples were dried to constant weight *in vacuo* at 45°. Gravimetric determinations of chlorine, as silver chloride, and sulfur, as barium sulfate, were carried out by the Parr peroxide bomb method.[9]

Cuprammonium study. The viscosity of 1% solutions in cuprammonium solution (200 g. ammonia and 15.0 g. copper per liter) ranged from 1.80–3.62 centipoises for samples A, B, C, and E. After purification with chlorite, samples A′, B′, and C′ gave values ranging from 1.80–2.48 centipoises.

Hydrolysis study. Samples (0.1–0.15 g.) of chlorocelluloses were dispersed in 2.00 ml. of 72% sulfuric acid (previously cooled to 12–15°) after 2 hr. at 18–20°. Sulfur dioxide was evolved during this period. Each solution was diluted to 3% acid and boiled under reflux for 4 hr.; in some cases material precipitated on dilution and remained insoluble during subsequent boiling. The cooled and filtered solutions were neutralized with barium carbonate, refiltered, acidified with acetic acid to a litmus endpoint, and concentrated to a thick sirup (0.1–0.2 ml.) *in vacuo* at 50°.

Paper chromatography. Chromatograms of each concentrated hydrolyzate were run on Whatman No. 1 filter paper in 10:3:3 butanol-pyridine-water for 12–72 hr., and sprayed with aniline–hydrogen phthalate reagent.

Cellulose chromatographic column. A sirup (2.35 g.) concentrated from a large scale hydrolyzate of A was placed on a developer-saturated Whatman standard grade cellulose powder column (22 × 2.25 in.). The developer solution, butanol half-saturated with water, was allowed to flow at a rate of 140 ml. per hr. for the first 700 ml., then at 20–25 ml. per hr. thereafter. The effluent was collected in fractions,[10] and the fractionation followed by means of paper chromatograms. The column was finally washed with 1200 ml. of 50% ethanol. All fractions were evaporated to constant weight *in vacuo* at 50°.

Identification of glucose. Glucose was crystallized from fraction 6–1 by seeding the concentrated decolorized sirup. The isolated crystals melted at 145°, and exhibited rotation in water of $[\alpha]^{25}_D$ +52°; the phenylosazone m.p. 204–205°. A mixture of the isolated compound and D-glucose m.p. 145°.

Identification of a monochloroglucose. Crystalline fraction 2 melted sharply at 134–135°, reduced Fehling solution strongly, and formed only small quantities of silver chloride when treated with silver nitrate solution. It showed a rotation in absolute ethanol of $[\alpha]^{25}_D$ $+100 \pm 3°$ (*c* 0.5) and in water a rotation of $[\alpha]^{25}_D$ $+43 \pm 3°$ (*c* 0.5). Helferich and Bredereck[11] found that 6-chloro-D-glucose melted at 135–136°, reduced Fehling solution rapidly, and gave a rotation in water of $[\alpha]_D$ +35.0°.

Anal. Calcd. for $C_6H_{11}O_5Cl$: C, 36.28; H, 5.58; Cl, 17.85. Found: C, 36.82; H, 5.85; Cl, 18.66.

RESULTS AND DISCUSSION

Upon addition of thionyl chloride to mixtures of cellulose and pyridine, an exothermal reaction takes place, and the mixture gradually darkens. This color effect increases with increasing tempera-

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(4) P. Carré and P. Mauclère, *Compt. rend.*, 192, 1567 (1931).

(5) This material was supplied by courtesy of Dr. M. Heath of The Buckeye Cellulose Corp., Memphis, Tenn. The degree of polymerization was calculated from the viscosity of a 2.5% solution in cuprammonium according to the ACS method (conversion chart 803-2M published by Hercules Powder Co.).

(6) H. R. C. Pratt, British Patent 538,028 (July 17, 1941); *Chem. Abstr.*, **36**, 1744; D. L. Cottle, *J. Am. Chem. Soc.*, **68**, 1380 (1946); L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., especially p. 367–368, Heath, New York, 1941.

(7) G. Jander, B. Gruttner, and G. Scholz, *Ber.*, **80**, 279 (1947).

(8) P. F. Cundy and M. M. Beck, *Paper Trade J.*, **124**, 18, 36 (May 1, 1947).

(9) *Peroxide Bomb: Apparatus and Methods*, Manual No. 121, Parr Instrument Co., Moline, Ill., 1950, p 47.

(10) L. Hough, J. K. N. Jones, and W. H. Wadman, *J. Chem. Soc.*, 2511 (1949).

(11) B. Helferich and H. Bredereck, *Ber.*, **60B**, 1995 (1927).

TABLE I

DESCRIPTION OF CHLOROCELLULOSES

Product	A	A′[a]	B	B′	C	C′	D	E
Reaction temp., °C.	26		50		69		25	25
Reaction time, hr.	4		4		1		4	4
Reaction ended with	NaOH		NaOH		NaOH		$NaHCO_3$	MeOH
Chlorine, %	6.12	6.96	12.90	13.50	19.66	20.16	4.42	5.23
Sulfur, %	0.70	0.13	2.30	0.30	2.04	0.93	4.86	11.65
Chlorine, D.S.[b]	0.29	0.33	0.67	0.67	1.04	1.04	0.22	0.30[c]
Sulfur, D.S.[b]	0.04	0.01	0.13	0.02	0.12	0.05	0.27	0.73[c]
Yield, based on A, B, and C, resp.		96.8		83.0		84.4		
Carbon, %		43.67		42.43		41.26		
Hydrogen, %		5.42		4.86		4.43		
Ash, %	0.09	0.08	0.08	0.20	0.10	0.27		
Material not dissolved by acid hydrolysis, %		None		4.9		8.3		

[a] A′, B′, and C′ represent A, B, C, respectively, after purification with chlorite. [b] The D.S. (degree of substitution) of the chlorocelluloses were calculated from the following simultaneous equations.

$$\text{Sulfur, } \% = 3206x/(162.1 + 46.04x + 18.45y)$$
$$\text{Chlorine, } \% = 3546y/(162.1 + 46.04x + 18.45y)$$

where y = degree of chlorine substitution, and x = degree of sulfite ester substitution (—OSOO—). [c] Treatment of sample E with 0.15*N* NaOH at 25° gave a 76% yield of material, analyzing for 6.44% chlorine and 0.62% sulfur, or D.S. of 0.31 and 0.04, respectively.

TABLE II

CHROMATOGRAPHIC FRACTIONATION OF HYDROLYZATE A

Fraction	R_g[a]	Dried Fraction, G.	Specific $[\alpha]_D^{25°}$	Rotation Solvent	Cl, %	Cl in Fraction, G.	Fehling's Test	$AgNO_3$ Test
1	4.3	0.0163	0	Abs. EtOH	13	0.0021	+	−
2	3.5	0.1303	+41.0 ± 0.4	Abs. EtOH	11.7	0.0152	+	−
3	2.7	0.0677	+13 ± 1	Abs. EtOH	11.2	0.0075	+	−
4	1.8	0.0402	+2 ± 1	Abs. EtOH	13.5	0.0054	+	+
5-1[b]	1.3	0.0803	−41 ± 1	H_2O	4.9	0.0039	+	−
5-2	1.3	0.0154	−3 ± 3	Abs. EtOH	6.4	0.0010	−	−
6-1[c]	1.0	1.1086	+40.2 ± 0.4	H_2O	1.48	0.0164	+	−
6-2	—	0.2071	0	EtOAc	0.4	0.0008	sl. +	−
7	Column Wash	1.6104	+2.9 ± 0.1	H_2O	2.12	0.0341	+	+
Total		3.2763				0.0864		
Residual[d]		0.594			8.9	0.053		
Original[e]		3.870			3.59	0.139		

[a] The R_g value is the rate of movement relative to the rate of movement of glucose. [b] Only a portion of fraction 5 was soluble in water (5/1), and the remainder (5/2) was soluble in ethanol. [c] Only a portion of fraction 6 was soluble in water (6/1), and the remainder (6/2) soluble in ethyl acetate. [d] This is the material (calculated by difference) remaining on the column after washing with 50% ethanol. [e] The original hydrolyzate contained 1.52 g. barium acetate and 2.35 g. hydrolyzed product.

ture. Thionyl chloride and pyridine alone also react exothermally, to form a dark solid which may be responsible for the color of the fibrous products. The chlorine content of chlorocelluloses increases with increased reaction time and temperature. Excessive reaction temperatures, however, result in the formation of black gritty nonfibrous materials.

The reaction is best terminated by treating the crude products with dilute alkali, which reduces the sulfur content to a small value. Further treatment with acidic sodium chlorite removes more sulfur and gives a lighter color to the product. The residual sulfur appears to be present as sulfurous acid esters, since sulfur dioxide is evolved upon treatment with 72% sulfuric acid or 85% phosphoric acid.

All the chlorocelluloses, except those with high chlorine content, appear to be largely soluble in cuprammonium solution. Only small amounts of material can be regenerated from these solutions, however. The viscosities of the solutions are extremely low, so it is evident that the chlorination of cellulose with thionyl chloride in pyridine is also a strong degrading action.

The chlorine in the chlorocelluloses seems to be firmly bound, as shown by acid hydrolysis; only traces of silver chloride are formed when the acidic solution is treated with silver nitrate and nitric acid. Resistance to hydrolysis increases as the chlorine content of the chlorocelluloses is increased, as shown by a larger amount of insoluble material in the hydrolyzate. Paper chromatography of the hydrolyzates gives spots for cellobiose and glucose, and also five additional spots of higher R_f value. The intensity of the glucose spot diminishes as the chlorine content of the original chlorocellulose is increased.

The hydrolyzate of a large sample of A was fractionated on a cellulose column and the data are presented in Table II. The presence of glucose in fraction 6–1 was definitely established, amounting to 47% of the total hydrolyzate. This large amount of glucose is commensurate with the low degree of chlorine substitution (0.29) of the original sample.

The resistance of chlorocelluloses to hydrolysis is again shown by the presence of two incompletely hydrolyzed components (fraction 7 and the residual material on the column), which contained 63% of the chlorine originally present in hydrolyzate A.

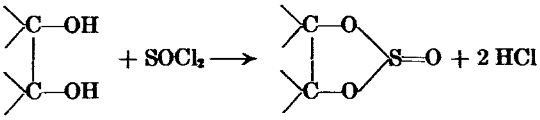
Fractions 1 through 4 possess chlorine contents slightly below the theoretical amount (17.85%) required for a monochlorohexose; they represent 22% of the chlorine originally present in the hydrolyzate. Attempts to obtain crystalline compounds from these fractions were largely unsuccessful. Gradual addition of petroleum ether (b.p. 30–60°) to an ethyl acetate solution of fraction 2 finally gave crystalline needles, analyzing for a monochlorohexose, and tentatively identified as 6-chloro-D-glucose.

Terminating the original chlorination reaction by soaking the products in either aqueous sodium bicarbonate or in methanol gave products with much higher sulfur contents (D and E in Table I). Treatment of the methanol-soaked product with dilute alkali (E) gave a product with a much reduced sulfur content; the chlorine content, when calculated as degree of substitution, showed no change. Acidification of the alkaline solution gave an evolution of sulfur dioxide. So it seems possible that the sulfur in these crude chlorocelluloses exists as cyclic sulfites, probably linked in either the 2,3- or 3,6-position, and of low stability.

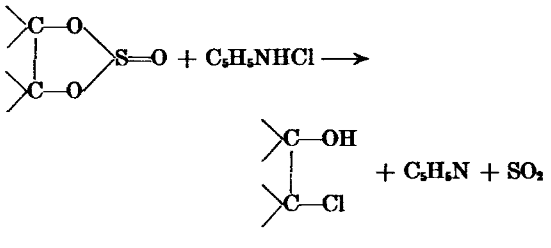
A mechanism for chlorination occurring during tosylation has been suggested by Hess and Stenzel,[12] the formation of a tosyl ester precedes chlorination, and pyridinium chloride, rather than the sulfonyl chloride is the chlorinating agent (reaction 1).

$$ROSO_2C_7H_7 + C_5H_5NHCl \longrightarrow RCl + C_5H_5NHSO_3C_7H_7 \quad (1)$$

A similar type of mechanism applied to chlorination with thionyl chloride and pyridine would suggest the formation of a sulfite ester, probably from carbons 2 and 3, or carbons 3 and 6, as a first step (Equation 2), and then a subsequent chlorination step with pyridinium chloride, leading to the formation of either a chlorohydrin (Equation 3) or a dichloro derivative. It is interesting that none of the fractions isolated from the chlorocellulose hydrolyzate (Table II) has sufficient chlorine to be considered a dichloro derivative; hence reaction 3 must predominate.



(2)



(3)

Several workers have reported the formation of cyclic sulfites from polyhydroxy compounds. Price and Berti[13] prepared both the cis and trans forms of the 1,2-cyclohexandiol sulfites, using a mixture of thionyl chloride and pyridine as reagent. No chlorination was reported in this reaction. De la Mare and co-workers[14] prepared 3-chlorotrimethylene sulfite, using thionyl chloride and a neutral solvent. When pyridine was used as the solvent, chlorination resulted, with the formation of a mixture of dichlorohydrins and trichloropropane. This again emphasizes the possible role of pyridinium chloride as the chlorinating agent, and the intermediate role of a sulfite ester.[15]

A second mechanism postulates the formation of an unstable chlorosulfite ester as an intermediate, and involves the attack of only one hydroxyl group (Equations 4 and 5). This has been investigated in detail for simple alcohols by Ingold and co-workers,[16] by Lewis and Boozer,[17] and by Cram.[18] Studies with stereoisomers have shown that an S_N1 mechanism gives retention of configuration, whereas inversion occurs with the S_N2 mechanism. In some cases a mixture of retention and inversion has been observed. Most of the reactions have been

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(12) K. Hess and H. Stenzel, *Ber.*, **68**, 981 (1935).

(13) C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1211 (1954).

(14) P. B. D. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchards, and D. Watson, *J. Chem. Soc.*, 1813 (1956).

(15) A recent patent [German Patent 875,804, *Chem. Abstr.*, 52, 9196e] gives the preparation of pentaerythritol dichlorohydrin sulfurous acid ester from the polyol and thionyl chloride in pyridine. This compound, purified by distillation *in vacuo* to a solid, m.p. 30°, was converted by hot alcoholic potassium hydroxide to the dichlorohydrin, m.p. 75–80°.

(16) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1267 (1937).

(17) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 308 (1952).

(18) D. J. Cram, *J. Am. Chem. Soc.*, **75**, 332 (1953).

$$ROH + SOCl_2 \longrightarrow ROSOCl + HCl \qquad (4)$$

$$ROSOCl \longrightarrow RCl + SO_2 \qquad (5)$$

carried out in thionyl chloride, without the use of pyridine, and the chlorosulfite esters have shown very low stability, in contrast to the cyclic sulfite esters formed from glycols and the sulfur groupings encountered in the present work. The isolation of products D and E, with a higher degree of sulfur substitution than of chlorine substitution, seems to be evidence against the presence of chlorosulfite esters in the chlorocelluloses.

Since only three isomeric monochloroglucoses (2-, 3-, and 6-) are possible, the isolation of four isomers from a chlorocellulose hydrolyzate raises the possibility of Walden inversion on either carbon 2 or 3 to give a monochloromannose or aldose. This type of alkyl-oxygen fission can occur either by reaction 3 or reaction 5. There is also a possibility of 2,3- and 3,6-anhydro derivatives being formed, either with or without chlorine. The latter possibility is shown by the isolation of three crude fractions (5–1, 5–2, and 6–2) with low chlorine contents. Ohle and co-workers[19] have reported the isolation of a 3,6-anhydro-1,2-isopropylidene-5-*O*-tosyl-D-glucose by the action of tosyl chloride and pyridine on 1,2-*O*-isopropylidene-D-glucofuranose.

Assuming that each sulfur atom in a chlorocellulose is linked to three oxygen atoms as a sulfite ester, it can be calculated that the empirical formulas of chlorocelluloses A, B, and C contain 0.6, 0.86, and 0.77 oxygen atoms in excess of the number necessary to combine with hydrogen as hydroxyl groups. This is a further indication of the possible presence of anhydro-ring formation.

Acknowledgments. Gratitude is expressed to B. L. Browning and members of the analytical group of The Institute of Paper Chemistry for the carbon and hydrogen determinations reported herein. This paper represents a portion of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence College, Appleton, Wis., June, 1953. This work was done under the direction of John W. Green.

APPLETON, WIS.

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[19] H. Ohle and E. Dickhauser, *Ber.*, **58**, 2593 (1925); H. Ohle, L. von Vargha, and H. Erlbach, *Ber.*, **61**, 1211 (1928).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, ABERDEEN]

Acid-Catalyzed Rearrangements in the Nepenthone Series

K. W. BENTLEY AND J. C. BALL

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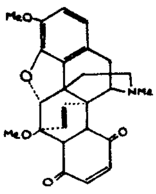
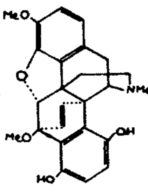
Thebaine on condensation with phenyl vinyl ketone affords a Diels-Alder adduct, nepenthone,[1] which has been rearranged in acid solution. Reduction affords nepenthol, which has been dehydrated to an olefin, nepenthene, and both nepenthol and nepenthene have been rearranged to flavonepenthone, an analog of flavothebaone. Mechanisms are advanced for the changes reported.

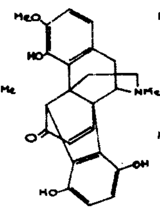
Thebaine, on condensation with *p*-benzoquinone affords the adduct (I)[2,3] which can be isomerized by acids to the quinol (II), and this on heating with hydrochloric acid undergoes a concerted opening of the cyclic ether and 1:2-shift of the quinol nucleus, giving flavothebaone[3–5] which has the structure (III).[4,5] During work on the structure of the last named base attempts were made to effect a similar rearrangement in somewhat simpler compounds.



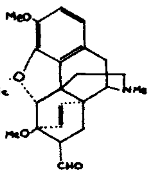
(I)



(II)



(III)



(IV)

The simplest thebaine adduct reported in the literature is thebaine-acrolein (IV),[6] but attempts to rearrange this in acid solution led to the immediate production of black intractable materials. The adduct of thebaine and phenyl vinyl ketone (V) was obtained from the two components in excellent yield, and was subjected to a variety of transformations. On account of the extremely

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[1] K. W. Bentley and J. C. Ball, *Chem. & Ind.* (*London*), 1428 (1956).

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