

compound was recrystallized from alcohol; yield 0.85 g.; m. p. 205–206°. ²¹

9,9-Di-(*p*-hydroxyphenyl)-anthrone-10.—To a solution of 2.0 g. of 9-hydroxy-9-(4'-hydroxyphenyl)-anthrone-10 in 10 cc. of hot phenol there was added three drops of concd. sulfuric acid. The mixture was heated for four hours on a steam-bath, the crystalline precipitate filtered through a warm funnel, recrystallized twice from dilute alcohol and then from acetic acid; yield 1.9 g.; m. p. 305–306° ²² with decompn.

9,9-Di-(*p*-methoxyphenyl)-anthrone-10.—After 1.0 g. of 9,9-di-(*p*-hydroxyphenyl)-anthrone-10, 50 cc. of 10% sodium hydroxide and 4 cc. of dimethyl sulfate had been stirred and heated for one hour on a steam-bath, the dimethoxy compound was obtained upon acidification; yield 0.9 g.; m. p. 206–207° ²³ after recrystallization from alcohol.

4'-Methoxydiphenylphthalin and Zinc Chloride.—A mixture of 18.0 g. of the phthalin, ²⁴ 5.4 g. of fused zinc chloride and 35 cc. of acetic anhydride was heated for five minutes on a steam-bath and poured into water which contained a small amount of hydrochloric acid. The gummy precipitate became solid when digested with water on a steam-bath. It was dissolved in 50 cc. of acetic acid, 9 g. of sodium dichromate added and heated for one-half hour on a steam-bath; 8.6 g. of crystalline product precipitated which was separated with the aid of acetic acid into 9-hydroxy-9-(4'-methoxyphenyl)-anthrone-10 (4.1 g.) which melted at 205–206° ²⁵ and 3-methoxy-9-hydroxy-

(21) Blicke and Weinkauff (*THIS JOURNAL*, **54**, 1462 (1932)) found 206–207°; ref. 4, m. p. 205–206°.

(22) Scharwin and Kusnezof (*Ber.*, **36**, 2020 (1903)) reported 308–309°.

(23) Scharwin, Naumof and Sandurin (*ibid.*, **37**, 3618 (1904)) found 208°.

(24) Ref. 13, p. 924.

(25) The same melting point is reported in the literature (ref. 4).

9-phenylanthrone-10 (0.5 g.) which was found to melt at 177–178°. ²⁶ Each product was purified by three recrystallizations from acetic acid.

4',4''-Dimethoxydiphenylphthalin and Zinc Chloride.—From 1 g. of the phthalin ²⁷ there was obtained 0.65 g. of yellow, crystalline 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran⁸; 0.5 g. of the furan yielded, upon oxidation, 0.4 g. of 2-(4'-methoxybenzoyl)-4'-methoxybenzophenone which melted at 157–158°. ²⁸

4',4''-Dichlorodiphenylphthalin and Zinc Chloride.—From 2 g. of the phthalin⁷ we obtained 1.6 g. of 3-chloro-9-(4'-chlorophenyl)-10-acetoxy-anthracene; m. p. 155–156° after recrystallization from acetic acid.

Anal. Calcd. for C₂₂H₁₄O₂Cl₂: Cl, 18.60. Found: Cl, 18.54.

Upon oxidation of 1.1 g. of the product there was produced 0.9 g. of 3-chloro-9-hydroxy-9-(4'-chlorophenyl)-anthrone-10; m. p. 222°. ²⁹

Summary

The action of zinc chloride and acetic anhydride on diphenyl-, 4'-hydroxydiphenyl-, 4'-methoxydiphenyl-, 4',4''-dimethoxydiphenyl- and 4',4''-dichlorodiphenylphthalin was studied. Oxidation of the initial reaction products yielded in one instance a 2-benzoylbenzophenone, in others hydroxy- or methoxyphenylanthrones.

(26) Ref. 4, m. p. 177–178°.

(27) Grande, *Gazz. chim. ital.*, **26**, 1, 228 (1896).

(28) Ref. 6, p. 1459, m. p. 157–159°.

(29) Ref. 7, p. 275, m. p. 223–224°.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 16, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 228]

The Preparation of Fibrous Iodo-cellulose Nitrates and the Probable Distribution of Nitrate Groups in Partly Nitrated Celluloses¹

BY G. E. MURRAY AND C. B. PURVES²

Although the average degree of substitution in partly nitrated celluloses can be calculated easily from the nitrogen content, no methods have been developed to determine the distribution of nitrate groups along the cellulosic chain or between the second, third and sixth positions of the individual glucose residues. This article is concerned with the latter aspect of the distribution and originated from a consideration of the work of others in the

(1) Presented at the Boston meeting of the American Chemical Society, September, 1939.

(2) This article is based on a thesis submitted by G. E. Murray to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1939.

methylglucoside series. The 2,3-dimethyl-4,6-dinitrate derivative of the latter gave a 70% yield of crude 2,3-dimethyl-6-iodomethylglucoside-4-nitrate when heated at 100° with sodium iodide in acetone.³ On the other hand, the 2,3,4-trinitrate gave a small amount of halogen-free product in the same conditions^{4a} while recrystallized 4,6-ethylidene methylglucoside 3-mononitrate was produced in 70% yield from the corresponding 2,3 dinitrate.^{4b} Although side reactions were obvious, it was clear that only nitrate groups in

(3) Irvine and Rutherford, *THIS JOURNAL*, **54**, 1491 (1932); Oldham, *J. Chem. Soc.*, 2840 (1925).

(4) Bell and Sygne, *ibid.*, (a) 1711 (1937); (b) 833 (1938).

primary alcoholic or sixth positions of the glucose residues were replaced by iodine. Those attached to secondary alcoholic positions might be removed but were not replaced. Cellulose nitrates have now been iodinated as extensively as possible and the analytical data interpreted in conformity with the results outlined above. The preliminary experiments were with guncotton, because its reaction with inorganic iodides could be studied in a homogeneous system.

Iodination of Guncotton (N, 13.2%).—One gram was dissolved in 100 cc. of solvent which had been dried over anhydrous potassium carbonate, boiled with sodium iodide and distilled. Upon the addition of 1 g. of anhydrous sodium, calcium or barium iodide, the solution developed a light yellow color that increased in intensity to a very deep red at the end of the run. Brown fumes were evolved and the viscosity, originally great, decreased rapidly. There was little change in color when zinc iodide was used. The product was precipitated by pouring the solution into rapidly stirred distilled water which, when necessary, contained a little sodium chloride to complete the coagulation. After purification by reprecipitation and washing with water or 50% aqueous methyl alcohol, the specimens were analyzed for iodine by a modification of the usual Carius procedure.⁵

The data (Table I) indicated that the optimum conditions for the replacement included an anhydrous medium, a ketone solvent, sodium iodide and a temperature of about 115°. These iodonitrates separated from solution in the usual trinitrate solvents as powders or gels rather than as fibers and had been extensively degraded by oxidative side reactions during their preparation.

TABLE I
THE IODINATION OF GUNCOTTON

Solvent	Iodide used	Hours of heating	Temp., °C.	% Iodine introduced
Methyl ethyl ketone	Na	12	80	2.75
Methyl ethyl ketone	Na	12	80	3.34 ^a
Methyl ethyl ketone	Na	12	80	2.41 ^b
Methyl ethyl ketone	Na	12	115	27.47
Methyl ethyl ketone	Zn	12	80	0.66
Methyl ethyl ketone	Zn	24	80	.20
Methyl ethyl ketone	Ca	12	80	2.58
Methyl ethyl ketone	Ba	12	80	2.79
Acetone	Na	12	56.5	0.0
Acetone	Na	12	105	2.03
Acetone	Na	12	115	24.7
<i>n</i> -Butyl acetate	Na	12	97	0.14
<i>n</i> -Butyl acetate	Na	2.5	97	.12
Ethyl alcohol	Na	12	115	.78
Acetylacetone	Na	12	115	23.8

^{a,b} Duplicate experiments except that (a) was anhydrous while (b) had 0.5% of water.

(5) Doering, *Ber.*, **70**, 1887 (1937).

(6) Cf. Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937).

As the amount of oxidation probably depended upon the degree of nitration, subsequent experiments were with lower nitrates. These were prepared with nitric acid-sulfuric acid mixtures containing much water,⁷ since nitration with nearly anhydrous mixtures was found too speedy to be interrupted at an intermediate stage.⁸

Partial Nitration of Cellulose.—High grade, purified cotton linters⁹ were kept in the standard nitrating mixtures⁷ at 15 to 20° with a ratio of 1 g. of cotton to 150 g. of acids. The products were isolated and stabilized by standard procedures. Nitrogen analyses were by the du Pont nitrometer and Dumas methods.

In one case, the nitric acid-sulfuric acid-water ratio was 37.4:35.4:27.2 parts by weight of anhydrous acids. The fibrous, insoluble product was isolated after one hour at 16° and had 4.8% nitrogen. It was further nitrated with a mixture (HNO₃, 18.7; H₂SO₄, 70.0; H₂O, 11.3%) which was used in a duplicate experiment with some of the original linters, presumably without degrading either sample. The viscosities of the two products (N, 13.32 and 13.17%) were determined in anhydrous *n*-butyl acetate at 25° for the concentration range 0.004 to 0.0004 mole per liter. Assuming 13.3×10^{-4} for Staudinger's K_m constant,¹⁰ the η_{sp}/c values, extrapolated to zero concentration, of 141 and 234 corresponded to chain lengths averaging 374 for the low nitrate and 626 for the original linters.

As the aqueous acid used in preparing these low nitrates caused substantial degradation, they probably contained cellulose chains of widely varying length. Their insolubility made it impracticable to use fractional precipitation methods^{11a} to study either the chain distribution or that of the substituents throughout the mass of the fiber. Although desirable in itself, such information was not required in the present research, which was devoted to differentiating between primary and secondary nitrate groups irrespective of their location in the cellulose. These low nitrates were accordingly considered to be reasonably fitted for the purpose in view, since they were fibrous and had considerable tensile strength.

Iodination of Low Nitrated Celluloses.—Two grams of dry sodium iodide was dissolved in 200 cc. of redistilled acetylacetone contained in a 500-cc. flask. An oil-bath raised the temperature to 115–120°, the dry, insoluble, partly nitrated cellulose was added (2 g.) and the heating at 115–120° continued with occasional shaking. The solution became deep red in color but no brown fumes

(7) Lunge and Bebie, *Angew. Chem.*, **14**, 486 (1901).

(8) Cf. Davidson, *J. Textile Inst.*, **29**, 195T (1938).

(9) We wish to thank Dr. C. W. Berl and the Hercules Powder Company for the gift of this material.

(10) Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag J. Springer, Berlin, 1932, pp. 498–512.

(11) Spurlin, (a) *Ind. Eng. Chem.*, **30**, 538 (1938); (b) *THIS JOURNAL*, **61**, 2222 (1939). The literature was reviewed and relative reaction rates discussed mathematically.

were evolved. The undissolved product, obtained in almost quantitative yield, was washed with reagent alcohol and exhaustively extracted with decinormal sodium thiosulfate solution to remove any adsorbed iodine. After a final washing with distilled water, the fibers were dried *in vacuo* over phosphorus pentoxide. As the presence of iodine caused nitrogen analyses by the Dumas or nitrometer methods to be invariably and seriously high, the Devarda alloy technique¹² was finally used, although the results of control experiments tended to be slightly low.

The iodo-cellulose nitrates ranged in color from white to deep brown with increasing iodine content, had some tensile strength and resembled the original fibrous nitrates under the microscope. Specimens prepared from purified ramie and containing about 5% nitrogen and 16% iodine were irradiated for twelve hours with the K_{α} line from a copper anode X-ray tube with a nickel filter in front of the beam. The distance from sample to film was 3.6 cm. and in front of the latter was an 0.002" aluminum foil filter to remove L radiation emitted by the iodine atoms. The diffraction patterns were fibrous in type but severe background radiation indicated some disorganization in the structure. Other samples of the same ramie were mercerized, nitrated to about 5% nitrogen and iodinated to varying degrees (I, 5–20%) while kept throughout under tension on glass frames. This increased the sharpness of the diffraction spots although the background was still heavy.

A specimen of iodo-cellulose nitrate with 20.8% of iodine and 1.4% of nitrogen was insoluble in acetylacetone, chloroform, *n*-butyl acetate, ethyl alcohol and glacial acetic acid. Pyridine caused some swelling but dissolution occurred only in cold, concentrated sulfuric acid with liberation of iodine and in 43% hydrochloric acid after long standing. Attempts to prepare soluble derivatives by nitration or by acetylation with pyridine and acetic anhydride were defeated by the instability of the iodo group. Selective reductions of either nitrate or iodine by a zinc-copper couple in glacial acetic acid, by cold, dilute hydriodic acid or by acid, neutral or alkaline sodium hydrosulfite were also unsatisfactory.

With the optimum conditions, the iodination of an insoluble cellulose low nitrate proceeded smoothly and the halogen content reached a maximum after twelve hours of heating (Table II).

TABLE II
THE RATE OF IODINATION OF A CELLULOSE NITRATE^a
(N, 5.08%)

Time, hr.	Iodine, %	Time, hr.	Iodine, %
0.25	1.80	4	12.2
.5	2.41	6	15.7
.75	4.20	8	18.0
1.0	5.50	12	20.4
1.5	5.00	16	20.4
2.0	8.20		

^a With excess sodium iodide in acetylacetone at 115–120°. Parallel experiments with sodium, barium, calcium and zinc iodides for twelve hours gave products with 20.4, 17.7, 4.5 and 0.35% iodine, respectively.

(12) Doré, "The Methods of Cellulose Chemistry," D. Van Nostrand Co., New York, N. Y., 1933, p. 232.

A series of nitrates ranging from 2.5 to 9.0% nitrogen were then iodinated to the maximum degree and the calculations summarized in Table III were made on the assumption that one mole of nitrate had been directly replaced by one halogen atom. The molar substitution per hexose unit (mol. wt. 162) of cellulose nitrate, x , was given by the relationship $(14x \times 100)/(162 + 45x) = \% N$ (Columns 1 and 2). After introducing the iodine, the molar amounts of this, y , together with that of the remaining nitrate groups, were obtained from the simultaneous equations $(14x \times 100)/(162 + 45x + 110y) = \% N$ and $(127y \times 100)/(162 + 45x + 110y) = \% I$ (Columns 3, 4, 5, 6). The data in Columns 2, 4 and 6 were then used to express the moles of nitrate replaced by iodine, those remaining and those lost without replacement as a percentage of the original degree of nitration (Columns 7, 8, 9).

Discussion of Results

If the third and the last two experiments of Table III are left out of consideration, about half of the original nitrate groups were replaced by iodine. This result held true for cellulose nitrates containing from 2.5 to 7.5% of nitrogen and was also independent of the amount of nitrate lost without replacement, which increased from 0.05 to 0.38 mole per glucose residue. As the severity of the oxidative side reactions probably depended on the latter figures, iodination and oxidation probably proceeded independently and halogen was not bound in unknown ways by partly oxidized regions in the insoluble fibers. The analytical data, of course, did not exclude an effect of this kind which was independent of the original degree of nitration but, if such occurred, it was also independent of the time of heating after the maximum amount of iodine had been introduced (Table II). This was considered to be unlikely. Moreover, if iodination was merely the replacement of superficial nitrate groups, then the percentage of those affected would have decreased steadily as the interior of the micelles became more highly nitrated. The fact that no such trend was observed for nitrates containing up to 7.5% nitrogen indicated that iodination and nitration (with mixtures containing much water) were reactions of the same type, *i. e.*, both were permutoid or both were superficial. The latter possibility could not be entirely excluded because the most highly nitrated cellulose considered had an average of 1.15 groups per hexose unit and these might be accommodated on the internal surface of the fiber.¹³ The simplest interpretation to place upon the data was to assume that iodine re-

(13) Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1931); Miles and Craik, *J. Phys. Chem.*, **34**, 2607 (1930).

TABLE III
THE RATIO OF PRIMARY TO SECONDARY NITRATE GROUPS IN PARTLY NITRATED CELLULOSES^a

Original nitrate		Iodinated nitrate				Moles of original nitrate		
(1) N, %	(2) Moles	(3) % I	(4) Mole	(5) % N ^b	(6) Mole	Replaced by I	Remaining	Lost
						(7) %	(8) %	(9) %
2.49	0.315	11.1	0.160	0.67	0.101	51	32	17
4.79	.656	22.4	.337	1.13	.171	51	26	23
4.94	.680	28.6	.506	0.92	.150	74 ^c	22	4
5.08	.704	20.8	.343	1.39	.225	49	32	19
5.08	.704	20.4	.337	1.57	.231	48	33	18
5.08	.704	23.4	.393	1.18	.183	55	26	19
6.60	.970	25.9	.468	2.13 ^d	.349	48	36	16
7.51	1.15	30.1 ^f	.548	1.30	.219	48	19	33
8.38	1.32	28.4	.486	2.54	.211	35 ^e	16	49
9.00	1.46	33.5 ^f	.609	0.97	.527	42	36	22

^a Iodinations with excess sodium iodide in acetonylacetone at 115–120° for twelve hours. ^b Estimated by Devarda alloy method. ^c A duplicate of preceding experiment. Omitted from average. ^d Estimated by Dumas method and almost certainly high. ^e Iodination incomplete. Omitted from average. ^f Iodination for sixteen hours.

placed primary alcoholic nitrate groups in cellulose as well as in the methylglucoside series^{3,4} and that in both cases secondary nitrate radicals were either unaffected or took part in oxidative side reactions. Half of the substitution caused by the more aqueous nitrating mixtures occurred in the primary or sixth positions of the cellulose chains and more than half if some primary nitrate groups happened to be removed instead of replaced during iodination. The insolubility of the iodocellulose nitrates and the unsatisfactory character of their derivatives prevented the support of these inferences by a definite chemical proof.

If the above tentative conclusions are entertained, it follows that, in any one of the nitrating systems used, the equilibrium



for primary alcoholic radicals lies at least as far to the right as those for the two secondary hydroxyls combined.^{11b} This is compatible with the view that the two types of hydroxyl are deesterified at approximately the same rate while the reverse process is more rapid with primary ones.¹⁴ All the equilibria move to the right with more anhydrous nitrating conditions and the ratio of primary to secondary nitrate decreases from about one-half for low nitrates to a limiting value of one-third for cellulose trinitrate. A plot of the molar amounts of primary against secondary nitrate groups, including data for cellulose (0,0), the de-

rivatives in Table III and the trinitrate (1,2), suggests that the nitration of primary, but not secondary, hydroxyl groups is practically complete in the pyroxylin.

The authors are greatly indebted to Dr. H. M. Spurlin for a private communication in which the tentative, rather than the final, nature of the above inferences was stressed. They also thank Professor B. E. Warren and Mr. J. Biscoe for valuable advice and the use of equipment during the X-ray work.

Summary

1. Sodium iodide in a ketone solvent at 115–120° removed a portion of the nitrate groups from cellulose nitrate and replaced another portion by iodine. The iodo-nitrates prepared in a heterogeneous reaction from partly nitrated cotton (N, 2.5–9.0%) contained up to 33% iodine and 0.7 to 2.5% of nitrogen. They were white, changing to brown in color with increasing iodine content, were insoluble in water and organic solvents, had some tensile strength and gave a fibrous but somewhat disorganized X-ray diffraction pattern.

By analogy with similar work in the methylglucoside series, the iodine was considered to have entered primary alcoholic positions of the cellulose chain exclusively. The simplest, but not necessarily the correct, explanation of the analytical data was then found in the inference that at least one-half of the nitrate groups in low cellulose nitrates were attached to primary hydroxyls.

(14) Cf. Cramer and Purves, *THIS JOURNAL*, **61**, 3458 (1939).