clinical-size fractions still give a higher ratio of 1,6′- to non-1,6′-linkages, with the possible exception of dextran B-512. Several possible explanations could be advanced to account for the usual increase in ratio. For example, molecular heterogeneity may have existed in the original dextran,[15b] the degradation changing the properties sufficiently to permit a fractionation on the basis of structure which was not accomplished before hydrolysis. In the absence of fractionation on a structural basis, hydrolysis of non-1,6′-linkages will in most cases cause an increase in apparent ratio, regardless of whether the hydrolysis rate constant of non-1,6′-linkages or the relative number broken were higher or lower than for 1,6′-linkages. Thus, there is a multiplicity of factors which may influence the apparent ratio for the isolated fraction. The absence of a significant change in the ratio for dextran B-512[15a] undoubtedly reflects the relatively small proportion of non-1,6′-linkages present and the resulting fact that most of the degradation of the polymer would be as a result of hydrolysis of 1,6′-linkages, for which no change in formic acid production would be obtained on the corrected basis.

The calculation of maximum and minimum DP_N from the periodate oxidation data on the original dextran and the isolated fraction, using equations 1 and 3, is of interest as further evidence of whether the fraction is a result of a relatively homogeneous-type cleavage. The clinical-size fraction from dextran B-512 has a DP_N between the calculated extremes and, therefore, could be a product of an essentially homogeneous cleavage. The observed values for the other three products, Table I, are significantly higher than the calculated maximum DP_N. This suggests a departure from homogeneous-type cleavage or a fractionation of the products on the basis of structure. Evidence from other studies[12] indicates that at least one contribution to the results is the fact that apparently removal of external branches by cleavage of non-1,6′-linkages leads to the formation of D-glucose and some oligosaccharides, which then are discarded in the isolation of the clinical-size fraction. While the same process apparently occurs with dextran B-512, it represents a minor part of the total bond cleavage[6] and has little influence on the periodate oxidation properties of the product.

PEORIA, ILLINOIS

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY AND THE BALLISTIC RESEARCH LABORATORIES OF ABERDEEN PROVING GROUND]

The Controlled Thermal Decomposition of Cellulose Nitrate. I[1,2]

BY M. L. WOLFROM, J. H. FRAZER, L. P. KUHN, E. E. DICKEY, S. M. OLIN, D. O. HOFFMAN, R. S. BOWER, A. CHANEY, ELOISE CARPENTER AND P. MCWAIN

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The thermal decomposition of propellant cellulose nitrate (12.6% N), under ignition conditions, has been investigated at 2–3 mm. A solid residue is formed which has been characterized analytically and which on denitration and hydrolysis yielded cellobiose, D-glucose, D-gluconic acid, D-erythrose and glyoxal. These results establish the material as a fragmented type of oxycellulose nitrate of an extremely low degree of polymerization. The results are interpreted on the basis of homolytic bond scission.

Since the initial preparation of cellulose nitrate by Pelouze[3] in 1838 and the recognition of its military importance by Schönbein[4] in the following decade, there has been an increasing amount of research on the decomposition of this substance. The action of chemical agents such as acids, bases and reducing substances has been investigated under a variety of conditions; a number of simple and a few complex reaction products have been identified.[5] A list[6] of the substances produced by the chemical agents follows (to provide comparison with those afforded by thermal decomposition): inorganic nitrites and nitrates; nitrogen[7]; cyanide[8]; oxides of nitrogen (N_2O,[7] NO[7] and NO_2) and carbon (CO[7,8] and CO_2); ammonia[8]; oxalic, malic, formic,[8] glycolic, butyric, malonic, tartaric,[8] trihydroxyglutaric, dihydroxybutyric, hydroxypyruvic,[8] isosaccharinic and tartronic acids; glucose; modified and degraded celluloses[9] and their nitrates.

The thermal decomposition of cellulose nitrate at 108° has been found to produce carbon dioxide and monoxide, nitric and nitrous oxides, methane and nitrogen.[10] Hydrogen cyanide was found by

(1) This work was carried out under contract (OEMsc-1152 with the Office of Emergency Management, Office of Scientific Research and Development; W-33-019-ord-3978 and -6279, and DA-33-019-ord-11, -163, -727 and -1466 with the Ordnance Department, United States Army) by The Ohio State University Research Foundation (Projects 170, 212, 313, 402, 458, 496 and 589). Preliminary investigations were performed by D. O. Hoffman and Prof. R. C. Elderfield in the Department of Chemistry of Columbia University, New York, N. Y.

(2) M. L. Wolfrom, *Abstracts Papers Am. Chem. Soc.*, **127**, 9E (1955); preliminary paper.

(3) T. J. Pelouze, *Compt. rend.*, **7**, 713 (1838).

(4) C. F. Schönbein, *Phil. Mag.*, **31**, 7 (1847).

(5) J. Barsha, in "Cellulose and Cellulose Derivatives," "High Polymers," Vol. V, 2nd edition, E. Ott, H. M. Spurlin and Mildred W. Grafflin, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p. 751, gives an excellent review on the action of chemical agents on cellulose nitrate and cites many references to the original literature.

(6) References are cited only for the products not noted by Barsha in reference 5.

(7) A. Angeli, *Atti reale accad. Lincei*, **28**, I, 20 (1919), and *Z. ges. Schiess-u. Sprengstoffw.*, **17**, 113 (1922); S. N. Danilov and L. I. Mirlas, *J. Gen. Chem. (U. S. S. R.)*, **4**, 817 (1934); G. G. Giannini, *Gazz. chim. ital.*, **54**, 79 (1924).

(8) E. Knecht and B. R. Bostock, *J. Soc. Chem. Ind.*, **39**, 163T (1920).

(9) B. Rassow and E. Dörr, *J. prakt. Chem.*, **108**, 113 (1924); T. Tomonari, *Z. Elektrochem.*, **40**, 207 (1934); A. Nadai, *Z. physik. Chem.*, **136**, 289 (1928).

(10) R. Vandoni, *Compt. rend.*, **201**, 674 (1935).

Muraour[11] when cellulose nitrate was ignited in a confined space. When cellulose nitrate was heated until deflagration occurred, Trapani[12] obtained products which gave a color test (Rimini) for formaldehyde. The isolation of water[13] and hydrocarbons[14] from heated cellulose nitrate has been reported. Desmaroux and associates[15] describe the isolation of a fibrous residue containing nitrogen (*ca.* 50% yield) from the prolonged heating of cellulose nitrate (11.9, 12.8 and 14.0% nitrogen; nitrated ramie fiber) at 108° under reduced pressure which removed the gases produced from the sample. No further investigation of this residue was reported. Rideal and Robertson[16] investigated the thermal decomposition of cellulose nitrate at very low pressures and quantitatively measured the composition of the gases evolved; they found hydrogen and formaldehyde to be present.

Information concerning the decomposition of cellulose nitrate under conditions similar to those prevailing when it is used as a propellant would be most valuable. However, under normal and higher pressures, all of the products are gaseous and provide little information as to the chemical nature of the intermediate materials. In the present work, propellant cellulose nitrate has been ignited at a pressure sufficiently low to remove the gaseous decomposition products rapidly from the high temperature zone. There was then left a solid residue. The preparation and characterization of this material is the subject of the investigation herein reported.

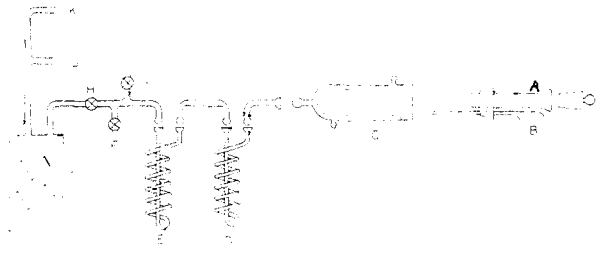


Fig. 1.—Apparatus for the thermal decomposition of cellulose nitrate: A, feeder tube, glass, 15 mm. o.d. with a 19/38 ground glass stopper; B, igniter, a double loop of No. 24 Chromel wire soldered to leads which were led through the rubber stopper and connected to a variable potential control; C, cold water-jacketed glass decomposition chamber, 25 cm. long inside, 3 cm. diam. inside at one end and tapered to a 28/15 glass ball joint at the exit end; D and E, spiral glass traps of 12 mm. o.d. tubing connected by 28/15 spherical joints and inserted into Dewar-held baths of solid carbon dioxide and acetone; F, vacuum release valve; G, stopcock to differential manometer; H, 15 mm. bore glass stopcock; I, surge tank, a steel pipe (0.3 × 1.3 m.) with gasketed fittings and flanges; J, take-off to a fine adjusting Meeker burner valve serving as a bleeder in adjusting pressure; K, connection to a high capacity Cenco Megavac pump protected by a glass trap cooled by a Dewar-held bath of solid carbon dioxide and acetone. The system was capable of maintaining a vacuum set at 2 mm.

The apparatus employed in preparing the material is shown in Fig. 1. It consisted essentially of a combustion chamber (C) attached to a large surge tank (I) and a high capacity vacuum pump. The propellant type cellulose nitrate, in the form of thin strips, was ignited in the combustion chamber with a hot wire after the pressure in the apparatus had been brought to 2–3 mm. The cellulose nitrate then underwent a self-sustained combustion, which, however, was incomplete and a solid residue remained in high yield (*ca.* 50%). This solid formed as a cloud of fine particles that had been ejected from the hot reaction sphere and had settled on the walls of the combustion chamber, from which they were removed. The material (product I, Fig. 2) was then subjected to a crude fractionation from methanol–water and the least soluble fraction (product II, Fig. 2) representing the least altered product, was employed for characterization.

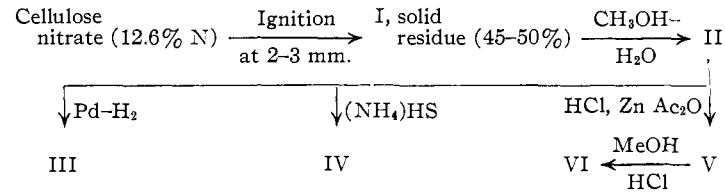


Fig. 2.—Product relationships.

Product II was an amorphous solid of a light yellow color that burned rapidly in air and left a carbonaceous residue. It was unstable toward moist air but could be stored in a dry atmosphere. Its heat of combustion and heat of explosion were measured (Table I) and were found to have changed from those of the initial material to the degree predictable from their difference in nitrogen content. A number average molecular weight, obtained by an ebullioscopic method, showed an average degree of polymerization of *ca.* 6. Since the material was undoubtedly highly heterogeneous, this number average will be grossly low.

TABLE I

HEATS OF COMBUSTION AND EXPLOSION OF THE SOLID CELLULOSE NITRATE (12.6% N) DECOMPOSITION PRODUCT

Substance[a]	Heat of combus.,[b] cal./g.	Heat of expl.,[c] cal./g.
Cellulose Nitrate (12.6% N)	2393	970[d]
Product I	2553–2583	542–638
Product II	2700–2732	683–685

[a] See Experimental part for preparation. [b] Determined under 10 atm. of oxygen. [c] Determined under 50 atm. of nitrogen. [d] Calculated.

Product II was characterized analytically (Table II) by elemental analysis and by assays for various functional groups. For the latter, the methods developed for oxycelluloses were adapted to the material at hand, which adaptation consisted principally in a correction for the inherent reagent instability of the products by extrapolation of rate curves

(11) H. Muraour, *Bull. soc. chim.*, [5] **3**, 265 (1936).
(12) E. Trapani, *Atti reale accad. Lincei*, **26**, I, 332 (1917).
(13) A. V. Saposhnikov, *J. Russ. Phys. Chem. Soc.*, **38**, 1186 (1906); *C. A.*, **1**, 1323 (1907).
(14) A. Koehler and M. Marqueyrol, *Mem. poudres*, **18**, 101 (1921); *C. A.*, **16**, 1866 (1922).
(15) J. Desmaroux, R. Vandoni, L. Brissaud and Therese Petipas, *Mem. poudres*, **29**, 134 (1939).
(16) E. K. Rideal and A. J. B. Robertson, "Third Symposium on Combustion and Flame and Explosion Phenomena," Williams and Wilkins Co., Baltimore, Md., 1949, p. 536.

to zero time. Thus there were found present significant amounts of carbonyl, carboxyl (mainly the uronic or keto acid type) and hydroxyl (in small part as a 1,2-glycol). An interesting point was that a definitive, low, non-ester methoxyl content was found, probably indicative of a partial glycosidation in the methanol made acid by the inherent acidity of the crude product I.

TABLE II

ANALYTICAL DATA FOR THE PRODUCTS OBTAINED BY THE THERMAL DECOMPOSITION OF CELLULOSE NITRATE UNDER LOW PRESSURE[a]

Constituent[b]	Constituent, % in Prod. II[c] (purif. decompn. solid)	Prod. III[c] (prod. II denitrated by H_2–Pd)	Prod. IV[c] (prod. II denitrated by NH_4HS)
C	28.5–29.3	43.2	..
H	3.4–3.7	6.4	..
Ash[d]	Trace	5.2	..
N (Dumas)	9.3–9.9	1.9	..
N (duPont nitrometer)	9.35	0.0	0.0
N (Kjeldahl)	..	1.5	..
OH[e] (total)	8.0	22.5	23.6
1,2-Glycol,[f] as OH	1.1	..	..
OR (glycosidic)	1.2 (OMe)	0.7 (OEt)	..
Carboxyl as CO_2	3.7[g]	..	1.8[g]
	3.2[h]	1.8[h]	..
Free carbonyl (aldehyde	2.4[i]	..	2.7[i]
and ketone), as CO	3.7[j]	4.5[j]	2.9[j]
S	..	..	5.0[k]
			5.8[l]
NH_3	..	..	1.7[m]

[a] 12.6% N cellulose nitrate; pressure 2–3 mm. [b] See Experimental portion for analytical details. [c] See Experimental portion for preparation. [d] Combustion residue; elementary data calculated to the ash-free basis. [e] By acetylation. [f] By lead tetraacetate oxidation; W. S. McClenahan with R. C. Hockett, THIS JOURNAL, 60, 2061 (1938); R. C. Hockett and W. S. McClenahan, *ibid.*, 61, 1667 (1939). [g] By decarboxylation. [h] By calcium acetate exchange. [i] By the Munson–Walker method, calibrated against D-glucose. [j] By oximation. [k] By iodine titration; M. P. Schubert, *J. Biol. Chem.*, 114, 346 (1936). [l] By oxidation to sulfate; W. F. Hoffman and R. A. Gortner, THIS JOURNAL, 45, 1033 (1923). [m] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 534.

The analytical data for product II were confirmed qualitatively by its infrared absorption spectrum (Fig. 3). A comparison of this spectrum with that of cellulose nitrate[17] (Fig. 3) shows the following changes: (a) the hydroxyl band at 3 μ has become stronger while the nitrate bands at 6.0, 7.8 and 11.8 μ have become weaker; (b) new bands have appeared at 5.75 and 6.35 μ. The 5.75 μ band undoubtedly can be ascribed to a carbonyl function (aldehyde, ketone, carboxyl or ester). On the basis of Kumler's data[18] on nitrated glycolate esters, the band at 6.35 μ may be indicative of a nitrate group on a carbon adjacent to a carboxyl function. The possibility that the band at 6.35 μ is due to a C-nitro group seems unlikely since the strong band for C-nitro at 7.25 μ[19] does not appear. Although neither the Dumas nor the nitrometer[20] assays distinguish between nitrate and nitrite nitrogen, the absence of significant amounts of nitrite ester groups is established since nitrite esters have strong bands at 6.1 and 12.7 μ,[20a] not present in Fig. 3. Product II exhibited a strong nitrate test (diphenylamine in sulfuric acid) and a faint nitrite test (with N,N-dimethylaniline, enhanced by the previous addition of alkali[5]). The latter is probably ascribable to a nitrate ester group in the α-position to a carbonyl or carboxyl group.[20b] The nitrogen content of product II had decreased to *ca.* 9.5% from the original content of 12.6%.

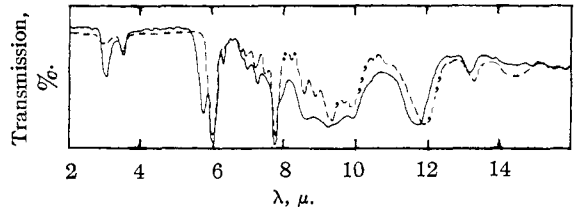


Fig. 3.—Infrared spectrum of cellulose nitrate (12.6% nitrogen), -----, and product II (Fig. 2), —. The spectra were determined using the method and instrument described in ref. 17.

The purified ignition residue (product II) was denitrated with palladium and hydrogen[21] to yield product III; by ammonium hydrogen sulfide to give IV; and, with considerable degradation, by reductive acetylation.[22] Analytical data obtained on products III and IV are shown in Table II. Denitration produces the expected large increase in hydroxyl value. Product II is a sensitive material and the denitration procedures effected unavoidable alterations in some of the functions present. Thus, in product IV, a considerable content of sulfur was found, perhaps, in part, as thiocarbonyl; likewise some ammonia nitrogen was present. The carboxyl content decreased markedly either by reduction of lactones or by decarboxylation. The isolation procedures may also have concentrated the less altered material so that the denitrated product fraction may not correspond exactly to the initial reactant fraction.

It was considered desirable to confirm and extend the analytical data on these products by actual degradative isolation work. This is a difficult problem for all oxycelluloses and especially so for one that contains nitrate groups. Product VI, obtained from the reductive acetylation of II with subsequent methanolysis, afforded methyl α-D-glucopyranoside after silicate column chromatography. After acetylation and subsequent silicate column chromatography, product VI also yielded α-cellobiose octaacetate. The denitrated product III was subjected to hydrolysis with sulfurous acid

(17) L. P. Kuhn, *Anal. Chem.*, **22**, 276 (1950).
(18) W. D. Kumler, THIS JOURNAL, **75**, 4346 (1953).
(19) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953).
(20) W. W. Scott, "Standard Methods of Chemical Analysis," 5th edition, N. H. Furman, Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 652.
(20a) P. Tarte, *Bull. soc. chim. Belges*, **60**, 240 (1951); *J. Chem. Phys.*, **20**, 1570 (1952).
(20b) L. P. Kuhn, unpublished work.
(21) L. P. Kuhn, THIS JOURNAL, **68**, 1761 (1946).
(22) D. O. Hoffman, R. S. Bower and M. L. Wolfrom, *ibid.*, **69**, 249 (1947).

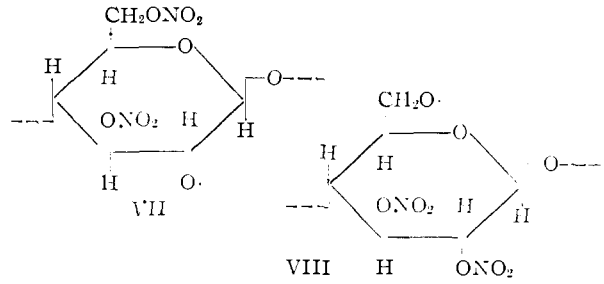
and from the hydrolyzate there was isolated directly D(?)-*arabino*-hexose phenylosazone,[23] also identified as the phenylosotriazole. Further reduction of product III (with hydrogen and Raney nickel) with subsequent acid hydrolysis, acetylation and silicate column chromatography, afforded D-glucitol (sorbitol; as the hexaacetate). Cautious hydrolysis of III, with dilute sulfuric acid, led to the isolation by column chromatographic methods, of D-gluconic acid (as the amide) and (after acetylation) of β-D(?)-glucopyranose pentaacetate.[23] The action of phenylhydrazine on this hydrolyzate with subsequent silicic acid column chromatography afforded D(?)-*glycero*-tetrose phenylosazone,[23] originating no doubt in a D-erythrose entity of the original II. From product II, and in much higher yield from product III, there was obtained on methanolysis with subsequent processing according to Grangaard, Gladding and Purves,[24] the bis-(2,4-dinitrophenylhydrazone) of glyoxal.

Consideration of the analyses and hydrolysis products obtained suggests that product II is a fragmented oxycellulose nitrate. Since both D-glucose derivatives and α-cellobiose octaacetate have been obtained in fair yield after denitration and hydrolysis, the polymer residue still contains intact anhydro-D-glucose entities. The origin of the other units can be related to the initial cellulose nitrate through a consideration of the mechanisms of the thermal decomposition of less complex nitrates.

Several recent investigations on the thermal decomposition of simple alkyl mononitrates have resulted in the belief that the initial step of the reaction is the homolytic cleavage of the O–N bond of the nitrate group with the formation of nitrogen dioxide and an alkoxyl radical, which react further.[25] The same initial cleavage has been suggested for the thermal decomposition of simple mononitrites.[26] The nitric oxide formed from the nitrites does not enter into subsequent reactions with the organic residues to the same extent that the nitrogen dioxide does. Kuhn and DeAngelis[27] have found that vicinal dinitrites undergo thermal decomposition with the formation of dialdehydes in which the bond between the carbons attached to the nitrite groups is ruptured; in particular, the formation of adipic dialdehyde from *trans*-1,2-cyclohexanediol dinitrite is of interest since a similar dinitrate group exists in the anhydro-D-glucose units of cellulose nitrate.

By analogy with simple nitrates, the homolytic cleavage of cellulose nitrate is believed to afford the intermediates VII and VIII.

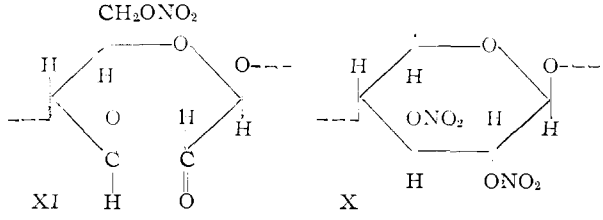
Another intermediate (from the cleavage of the nitrate group on carbon 3) is possible but, since it



VII VIII

would be expected to participate in any subsequent steps in a manner very similar to intermediate VII, it need not be of further concern.

Intermediate VII should cleave and eliminate nitrogen dioxide in the same manner described for the vicinal dinitrites to give a stable unit IX. The existence of the unit IX in product II has been con-

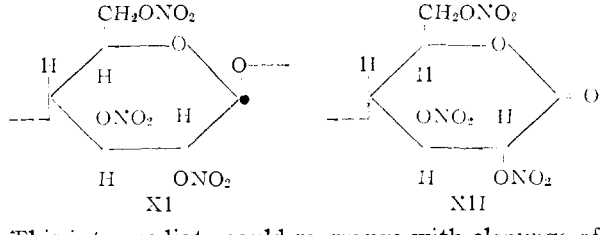


XI X

firmed by the isolation of two carbon atom (glyoxal) and four carbon atom (D-erythrose) molecules after denitration and hydrolysis.

A similar cleavage and elimination in VIII with the formation of formaldehyde and a new unstable intermediate X may be expected. Since a good yield of formaldehyde has been obtained from the thermal decomposition of cellulose nitrate at slightly higher pressure,[2] this reaction is considered probable. As no five-carbon fragment derivable from the intermediate X has been isolated, this intermediate may subsequently decompose, possibly with cleavage of the cellulose chain.

Another probable reaction that the intermediates VII and VIII may initiate is the transfer of a hydrogen atom from a carbon to the alkoxyl radical, the net result being the conversion of the original nitrate group to a hydroxyl group. If the hydrogen atom were removed from a carbon that was involved in the glycosidic bonds of the cellulose nitrate, an intermediate XI would be possible.



XI XII

This intermediate could rearrange with cleavage of the cellulose chain and formation of the unit XII at one of the new chain ends. This unit is a lactone and may explain the acidity and carboxyl content of product II. In addition, the D-gluconic acid derivatives which have been isolated after denitration and hydrolysis of product II may arise from this unit XII. If the hydrogen atom were removed from a carbon which held a nitrate group, elimination of nitrogen dioxide from the new radi-

(23) Although insufficient material was obtained to define the optical rotation, there is no reason to believe that the anhydro-D-glucose unit, initially present, had undergone any optical inversion.

(24) D. H. Grangaard, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **115**, No. 7, 71 (1942).

(25) G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.*, **45**, 494 (1949); L. Phillips, *Nature*, **160**, 753 (1947); **165**, 564 (1950); J. B. Levy, THIS JOURNAL, **76**, 3254, 3790 (1954).

(26) E. W. R. Steacie and W. M. Smith, *J. Chem. Phys.*, **4**, 504 (1936); F. O. Rice and E. L. Rodowskas, THIS JOURNAL, **57**, 350 (1935); N. Kornblum and E. Oliveto, *ibid.*, **71**, 226 (1949); J. B. Levy, *ibid.*, **75**, 1801 (1953).

(27) L. P. Kuhn and L. DeAngelis, *ibid.*, **76**, 328 (1954).

cal would afford a carbonyl group. Although color tests and analyses indicate carbonyl functions in product II, no definitive derivative which can be related to this function (containing six carbons) has been isolated.

All of the above processes require the formation of considerable amounts of nitrogen dioxide. Since nitrogen dioxide acts as an oxidizing agent, the major part of it is reduced to nitric oxide and the organic products are oxidized.[2,25] This action suggests alternative routes by which some of the functional groups in product II may arise. However, it is believed probable that under the experimental conditions employed, the oxidative effects of the nitrogen dioxide may be confined primarily to the organic products[2] other than product II.

The thermally initiated, near-explosive breakdown of the cellulose nitrate molecule would be expected to produce fragments which are most altered at the chain-breaking points. Thus, product II may consist of a central core of essentially unaltered nitrated anhydro-D-glucose units flanked at one or both ends by altered units which would account for the carbonyl and carboxyl contents as well as for the glyoxal and tetrose entities isolated on degradation.

Experimental

Preparation of Cellulose Nitrate Sheets.—The cellulose nitrate[28] employed was a blended propellant type containing 12.6% N (dry basis) and 35% water and having a viscosity specification of 8–20 sec. An amount of 100 g. of this moist cellulose nitrate was covered with abs. ethanol, stirred well, filtered and washed with abs. ethanol. The residue was submerged in abs. ethanol and, after standing overnight, was filtered and washed again. The dehydrated material was freed of most of the alcohol by filtration and was immediately shaken with 1 liter of ethyl acetate until homogeneous (about 2 hr.). The solutions were protected against moisture. After standing until free from entrapped air bubbles, portions (300 ml.) of the resultant solution were poured onto a glass plate (35 cm. square) supported over a layer of Drierite (soluble anhydrite, $CaSO_4$) in a drying box which was equipped with a steam coil for heating the plate and an inlet with three orifices for warm, dry air. After about 3 hr., during which time the temperature in the box was maintained at about 50°, the resulting clear flexible sheet (about 0.15 mm. in thickness; an occasional cloudy sheet was not used) was removed. Sheets which adhered firmly to the glass plate were removed with running water and dried between paper towels under pressure to prevent curling. No attempt was made to remove residual traces of solvent.

Cellulose Nitrate Decomposition.—A weighed amount of cellulose nitrate sheet was cut into 2 × 10 cm. strips which, when folded lengthwise, would fall onto the Chromel wire loop of the igniter (B, Fig. 1) on insertion through the feeder tube A. The feeder tube was closed and the pressure in the system was reduced to 2–3 mm. with a high capacity vacuum pump (Cenco Megavac). An electric potential (20–30 volts) was applied to the igniter until the glowing loop initiated decomposition of the cellulose nitrate strip whereupon the current was broken. Ignition invariably began at the points of contact of the sheet and hot wire and continued rapidly with little flaming. Although decomposition was completed within a few seconds, observation indicated that the decomposition radiated in all directions from a point of initiation. The decomposing edge was characterized by a puffy, foamy surface, only slightly discolored by charring, from which a grayish cloud of fine dust evolved. Infrequently, the decomposition was not self-sustaining, in which case the igniter was used to re-initiate the process. After a strip was decomposed, the stopcock H was closed and the vacuum in A–F was relieved by opening F. After each decomposition, the solid material (product I, Fig. 2) remaining in the chamber, C, was scraped out and stored under reduced pressure over phosphorus pentoxide and sodium hydroxide. The process was continued by closing the chamber, inserting a new strip at A, closing F, opening H slowly to evacuate the system to 2–3 mm. and then repeating the steps as above. The dry product was screened through a 16 mesh (per in.) sieve to remove undecomposed cellulose nitrate; yield of crude material, product I, 43–51 g. per 100 g. of cellulose nitrate sheet, $[\alpha]^{27}D$ +20° (*c* 3, methanol). The material was an amorphous solid of a light yellow tinge which exhibited many gas cavities when examined under the microscope. It was unstable toward prolonged exposure to moist air, evolving gases and changing to a soft brown material. Solutions in ethanol containing dry hydrogen chloride (0.25 *N*, *c* 2) and in ethanol–pyridine (1:1 by vol., *c* 3) showed no change in rotation over an observation period of 2–3 days at room temperature. Heating of the original cellulose nitrate fibers in mineral oil at 120° for 1 hr., while reducing the viscosity in solution, produced no observable effect on the decomposition product obtained.

After decomposition of a number of strips, traps D and E were removed from the system and placed in an ice–water-bath. After 1 hr., during which time some nitrogen oxides were evolved, a light brown liquid remained in the traps; yield 15–17 g. per 100 g. of cellulose nitrate sheet.

In one experiment a blended cellulose nitrate[29] containing 13.4% N was utilized; the ignition was not as self-sustaining and the yield (basis of 100 g. of cellulose nitrate sheet), 31.2 g. of solid and 20.6 g. of liquid, of desired product was lower.

Purification of the Cellulose Nitrate Solid Decomposition Residue.—Product I, 15 g., was dissolved in 100 ml. of methanol and the solution was decolorized with activated carbon (Darco G60), filtered through a bed of diatomaceous earth (Super-Cel, Johns-Manville) and added dropwise under mechanical stirring to 800 ml. of water. After 24 hr., the settled precipitate was removed by filtration, washed with water and pressed as dry as possible on the suction filter. After drying for several days over anhydrous calcium chloride, it was stored under reduced pressure over phosphorus pentoxide and sodium hydroxide; yield 7.5 g. (50%), $[\alpha]^{26}D$ +24° (*c* 3, methanol).

After pulverization in a mortar, this product was stirred with 60 ml. of dry ether for 1 hr. and filtered; yield of purified material, product II (Fig. 2) (residue after drying) 5.6 g. (75%), $[\alpha]^{28}D$ +22° (*c* 3, methanol) and +23° (*c* 3, acetone), n (solid) 1.512 ± 0.001 (1.510 is recorded for cellulose nitrate of the same nitrogen content.[30])

Product II was a nearly colorless, amorphous solid that gave solutions of a faint yellow color. When heated in a capillary tube, it softened at 145–160° and on continued heating evolved gases and darkened until at 170–180° a black residue remained. It burned rapidly on ignition in air and left a carbonaceous residue. It puffed mildly when heated rapidly in a test-tube. It could be stored indefinitely in the dry state under reduced pressure but was unstable toward moist air. It was insoluble in hydrocarbons, carbon tetrachloride, chloroform, and carbon disulfide, was slightly soluble in water and in ether at room temperature, and was soluble in the oxygenated solvents (such as alcohols, esters, acetic acid, ketones, dioxane and methylal) and in nitromethane, pyridine and dilute (2–4%) aqueous alkalies (sodium hydroxide, ammonium hydroxide and sodium carbonate). The ultraviolet absorption of product II in ethanol solution showed only end absorption with no characteristic bands; its infrared spectrum is shown in Fig. 3.

The relative viscosity of an acetone solution (*c* 1.9) of product II as determined in an Ostwald-type viscometer was 1.08 at 25°. The heats of combustion and of explosion are recorded in Table I.

A Cottrell boiling point apparatus similar to the modification of Spencer[31] was constructed and calibrated for acetone with benzoic acid. In this apparatus, product II yielded a molecular weight of 1500 ± 100 for 1–6% (by wt.) solutions in acetone. The plot of the weights of solute *vs.* the boiling point elevations was essentially a straight line.

Nature of the Nitrogen in the Cellulose Nitrate Solid Decomposition Residue.—A weighed amount (1 g.) of product

(28) Obtained from the Hercules Powder Co., Wilmington, Del.

(29) Obtained from the E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.

(30) K. Kanamaru, *Helv. Chim. Acta*, **17**, 1429 (1934).

(31) J. F. Spencer, THIS JOURNAL, **43**, 301 (1921).

II was transferred to the reaction bulb of a du Pont nitrometer with 20 ml. of concentrated sulfuric acid and the mixture of gases obtained was assayed for nitric oxide, carbon dioxide and carbon monoxide by successive absorption in acidic potassium permanganate, 50% potassium hydroxide, and cuprous chloride in dilute hydrochloric acid.

Anal. N (total, by Dumas), 9.7; N (nitrate, as above), 9.35; CO_2, 0.59; CO, 0.33; (see also Table II).

Product II gave a positive nitrate test[32] (deep-blue color with diphenylamine in concentrated sulfuric acid).

A method for assaying terminal glycosidic nitrate groups was established with tetra-*O*-acetyl-D-glucopyranosyl nitrate[33] by refluxing 0.2 g. of this substance for 30 min. with 1 g. of barium carbonate in 10 ml. of methanol, evaporating the mixture to dryness, dissolving the residue in 30 ml. of water and 8 ml. of glacial acetic acid, and precipitating the free nitrate ion with nitron[34]; 92% of the labile glycosidic nitrate group was so removed. Similar treatment of 0.6 g. of product II with an extended reflux time of 15 hr. resulted in finding a negligible amount (<0.04%, as N) of such a nitrate group. Several variations of the method of Murray and Purves[35] for the determination of primary nitrate groups were found to be inapplicable to product II.

Product I gave a strong nitrite test (liberation of iodine from acidified potassium iodide solution[36]). An aqueous extract of product II exhibited a weak nitrite test with the N,N-dimethylaniline reagent[37] which was greatly enhanced when the material was dissolved in 2–4% aqueous sodium hydroxide (as expected, see ref. 5). Both products I and II gave a negative color test[38] for the oxime grouping.

Denitration of the Cellulose Nitrate Solid Decomposition Residue.—Product II was denitrated according to the general procedure of Kuhn.[21] An amount of 2 g. of the material was dissolved in 95% ethanol, 10 g. of a 5% palladium-on-charcoal catalyst (Baker and Co., Inc., Newark, N. J.) was added and the mixture was shaken mechanically for 4 hr. with hydrogen at atmospheric pressure. The mixture was then free of nitrate and nitrite.[32,36] The catalyst was removed by filtration and was washed with 95% ethanol and with hot water. After solvent evaporation of the combined filtrate and washings under reduced pressure, the denitrated material, product III (Fig. 2), was recovered in high yield and was an acidic, amorphous, tan-colored solid. Alternatively, the filtrate was neutralized with ammonium hydroxide and the product was recovered as the ammonium salt.

Product II was also denitrated with ammonium hydrogen sulfide according to the technique which Bock and coworkers[39] employed for pectin nitrate. An amount of 20 g. of product II was dissolved in 200 ml. of abs. ethanol and 300 ml. of 95% ethanol, which was 1.75 *N* in ammonia and saturated with hydrogen sulfide at 13 ± 2°, was added dropwise to the solution while passing a slow stream of hydrogen sulfide through the mixture. After completion of the addition, the gas flow was continued for 1 hr. The reaction mixture changed from a clean light yellow to an orange-red color and a heavy, amorphous precipitate formed. After cooling overnight at 3–5°, the precipitate was filtered by suction and washed with cold 95% ethanol until the washings were colorless. The precipitate was suspended in water and the mixture made just acid to litmus paper with 0.5 *N* hydrochloric acid; the solid was removed by centrifugation and washed once with water. The supernatant liquor and washings were combined and concentrated under reduced pressure (5 mm.) to 80 ml. After filtration through a bed of barium sulfate and Celite (Johns-Manville), the solution was added dropwise under mechanical stirring to 500 ml. of abs. ethanol. The precipitate which had settled out on cooling overnight at 5° was centrifuged down, washed with cold 95% ethanol, and dried under reduced pressure over anhydrous calcium chloride; yield of denitrated material, product IV (Fig. 2), 7.6 g. Product IV (see Table II) gave a negative sulfide test with lead acetate but a positive test for a thiocarbonyl substance was obtained with Grote reagent.[40]

The reductive acetolysis procedure employing the hydrogen chloride catalyst of Hoffman, Bower and Wolfrom[22] was used to denitrate 5.0 g. of product II; yield after drying, product V (Fig. 2), 4.4 g. (viscosity, *c* 0.7 in acetone, 1.05 relative to acetone).

Product V was treated with a boiling solution of 3% hydrogen chloride in methanol for 18 hr. After treatment with silver carbonate, filtration and saturation with hydrogen sulfide, the solution was filtered and the solvent was removed from the filtrate under reduced pressure; yield of product VI, 2.6 g.

Qualitative Investigation of the Solid Cellulose Nitrate Decomposition Product.—Application of the cochineal test[41] to product II gave a positive oxycellulose test but no positive test for a hexuronic acid was obtained with several modifications of the naphthoresorcinol method.[42]

Products III–VI gave positive Molisch carbohydrate[43] tests (the nitrate in products I and II interferes), but negative results were obtained on all products with the Barfoed monosaccharide test.[44] Products III–VI (nitrate interferes) gave negative orcinol tests[45] for pentoses and positive Dische tests[46] for hexoses. Further evidence for the absence of pentoses was the negative aniline acetate test[47] on products III–VI.

Functional Group Assays on the Solid Cellulose Nitrate Decomposition Product. 1. Determination of Free Hydroxyl.—The general acetylative procedure of Malm, Genung and Williams[48] was used to determine the hydroxyl content of products II–IV (in some cases a ratio of acetic anhydride to pyridine as high as 7:1 was used to impede decomposition of the sample). In the determination of a blank, the same amount of sample material as was used in the determination proper was added to the blank hydrolyzate just prior to titration to account for the acidity in the sample. The results, together with those obtained below, are included in Table II.

2. Determination of Carboxyl.—(a) The carboxyl contents of products II and III were determined by the utilization of their reaction with aqueous calcium acetate according to the method of Lüdke[49] as modified by Yackel and Kenyon[50] except that the results were determined by extrapolation to zero time of a plot of the calcium consumption *vs.* time.

(b) Another method used for the determination of carboxyl in product II was that based on the Lefévre–Tollens assay[51] as modified by Whistler, Martin and Harris.[52] It was found that the procedure resulted in oxidative degradation due to the nitric acid generated from the nitrate ester groups in product II. Addition of stannous chloride eliminated this oxidative degradation but it was found (on pure D-galacturonic acid) that only 75% of the carboxyl groups were converted to carbon dioxide with this addition. The value obtained for product II was corrected by this factor.

3. Determination of Carbonyl.—(a) The method of Bryant and Smith,[53] as modified by Gladding and Purves,[54]

(32) R. K. McAlpine and B. A. Soule, "Prescott and Johnson's Qualitative Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1933, p. 477.

(33) W. Koenigs and E. Knorr, *Ber.*, **34**, 973 (1901).

(34) W. C. Cope and J. Barab, THIS JOURNAL, **39**, 504 (1917).

(35) G. E. Murray and C. B. Purves, *ibid.*, **62**, 3194 (1940).

(36) Reference 32, p. 473.

(37) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand Co., Inc., New York, N. Y., 1947, Vol. II, pp. 351, 355.

(38) F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., Inc., New York, N. Y., 1939, 2nd English edition, pp. 158, 290.

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(43) C. A. Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, N. Y., 1927, p. 114.

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(45) Reference 43, p. 179.

(46) Z. Dische, *Mikrochemie*, **7**, 33 (1929).

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(48) C. J. Malm, L. B. Genung and R. F. Williams, *Anal. Chem.*, **14**, 935 (1942).

(49) M. Lüdke, *Angew. Chem.*, **48**, 650 (1935).

(50) E. C. Yackel and W. O. Kenyon, THIS JOURNAL, **64**, 121 (1942).

(51) K. U. Lefévre and B. Tollens, *Ber.*, **40**, 4513 (1907); B. Burkhart, C. Bauer and K. P. Link, *J. Biol. Chem.*, **104**, 171 (1934).

(52) R. L. Whistler, A. R. Martin and M. Harris, *J. Research Natl. Bur. Standards*, **24**, 13 (1940).

(53) W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

(54) E. K. Gladding and C. B. Purves, *Paper Trade J.*, **116**, No. 14, 26 (1943).

was used on the calcium salts of products II and III except that a plot of the hydroxylamine consumption *vs.* time was extrapolated to zero time to correct for decomposition.

(b) The carbonyl content of product II was also determined by means of the Munson–Walker method,[55] in which carboxyl does not interfere. The various modifications of the aldose titration employing hypoiodite, such as the Cajori procedure,[56] were found to be inapplicable due to extensive decomposition by the alkaline reagents.

4. Determination of Alkoxyl.—The alkoxyl content of product II was determined (see Table II) by the Hoffman and Wolfrom[57] modification of the Vieböck and Schwappach[58] volumetric procedure. The alkoxyl was shown to be methoxyl by the method of Willstätter and Utzinger[59] which involves formation of the quaternary base with dimethylaniline and observation of the melting point. Treatment of product III (which contained 0.7% ethoxyl by the above procedures) with cold ($<-5°$) dilute sodium hydroxide did not cause a decrease in the alkoxyl content.

Isolation of Methyl α-D-Glucopyranoside.—Product VI, 1.1 g. of sirup, was dissolved in 35 ml. of methanol and adsorbed on a column (4.8 mm., diam., × 8.4 cm.) of Florex XXX and Celite (5:1)[60] and developed with 250 ml. of ethanol/water 70/30. The column effluent was evaporated to dryness under reduced pressure and the residue was chromatographed on Silene EF using dioxane/water 90/10 as the developer.[61] Two zones were obtained, one of which afforded a crystalline substance on evaporation of the eluate; yield 0.30 g. It was identified as methyl α-D-glucopyranoside, m.p. 164–166°, $[\alpha]^{23}D$ +154° (*c* 4.6, water), melting point unchanged on admixture with an authentic specimen of methyl α-D-glucopyranoside (m.p. 166° and $[\alpha]^{28}D$ +158°).

Isolation of α-Cellobiose Octaacetate.—Product VI, 5.0 g., was dissolved in a mixture of 45 ml. of acetic anhydride and 5 ml. of concentrated sulfuric acid. After 8 days at room temperature, the black reaction mixture was poured into water and the black, tarry precipitate was triturated with water until the product became easily friable; yield of dry, amorphous powder, 2.06 g. This product afforded four zones when chromatographed on Magnesol–Celite using benzene/ethanol 200/1 as the developer, according to the procedure of McNeely, Binkley and Wolfrom.[62] The second zone from the bottom yielded material, which, after recrystallization from 95% alcohol, gave *ca.* 0.1 g. of crystalline α-cellobiose octaacetate, m.p. 222–223°, $[\alpha]^{20}D$ +38.2° (*c* 4.3, chloroform); m.p. unchanged on admixture with known α-cellobiose octaacetate of m.p. 222–223° and $[\alpha]^{20}D$ +38.9°.

Isolation of D-Gluconamide.—Product III was converted to its barium salt by dissolving 5 g. in 100 ml. of hot water, adding an excess of barium carbonate (2.0 g.), filtering (precipitate washed with hot water) and concentrating the combined filtrate and washings to 15 ml. under reduced pressure. The concentrate was added dropwise, under mechanical stirring, to 400 ml. of abs. ethanol. The precipitate was removed by centrifugation, washed once with abs. ethanol and dried. The precipitated barium salt (2.7 g.) was dissolved in 2% aqueous sulfuric acid and heated at 100° for 5 hr. After filtration, the solution was treated with excess barium carbonate and the salts were precipitated again from ethanol as above. The dry salts were hydrolyzed again as described above, employing 5% sulfuric acid. After isolation, the salts were treated again with 5% sulfuric acid under reflux for 5 hr. The hydrolysis product was isolated as above and contained 25.1% Ba (calcd. for barium D-gluconate, 25.9%). The ethanol washes from the hydrolyses were combined and utilized as below.

The barium salt, 1.02 g. from the last hydrolysis above, was dissolved in water and treated successively with sulfuric acid, lead acetate and hydrogen sulfide. After filtration, the solution was evaporated to dryness under reduced pressure four times in succession with abs. ethanol to cause lactonization of the acids. The resultant friable mass was dissolved in 25 ml. of liquid ammonia and the ammonia was allowed to evaporate slowly.[63] The residue was chromatographed on Silene EF[61] using dioxane/water 90/10 as the developer. The material from the leading zone (3% based on product III) was identified as D-gluconamide, m.p. 135–140° dec., $[\alpha]^{21}D$ +30° (*c* 2, water); reported[64]: m.p. 145°, $[\alpha]D$ +31° (water). Acetylation afforded D-gluconamide pentaacetate, m.p. 185–186.5°, $[\alpha]^{25}D$ +23.2° (*c* 1.0, chloroform); m.p. unchanged on mixture with known material (m.p. 184–185°, $[\alpha]^{25}D$ +23.6° (*c* 0.9, chloroform)).[64]

Isolation of β-D(?)-Glucopyranose Pentaacetate.[23]—The ethanol washings, obtained above from product III, were evaporated to dryness under reduced pressure and the brittle solid was acetylated with acetic anhydride and fused sodium acetate. After isolation, the acetates were chromatographed on Magnesol–Celite.[62] One major zone was obtained and eluted. After crystallization from 95% alcohol, the product obtained was β-D(?)-glucopyranose pentaacetate; yield 26% (based on product III), m.p. 127–130° (accepted, 131°).

Isolation of D(?)-*glycero*-Tetrose Phenylosazone.[23]—An amount of 1.0 g. of the residue from the above ethanol washings and 1.0 g. of sodium bisulfite were dissolved in 50 ml. of water. A solution of 7.0 g. of sodium acetate in 20 ml. of hot water and another solution containing 4.5 g. of phenylhydrazine hydrochloride in 30 ml. of water were added in that order to the first solution. The solution was heated at 100° for 3 hr. and the precipitate was filtered, dried and extracted with hot benzene. The benzene solution was chromatographed on silicic acid–Celite[65] using petroleum ether (b.p. 91–96°)/abs. ethanol 25/1 as the developer. The material from the second zone from the bottom was rechromatographed 3 times and crystallized from ethyl acetate as yellow prisms, m.p. 161–165°. An authentic sample of D-*glycero*-tetrose phenylosazone was prepared,[66] m.p. 165–167°, mixed m.p. 161–166°. Insufficient material was obtained for further characterization.

Isolation of D(?)-*arabino*-Hexose Phenylosazone.[23]—A 50-mg. sample of product III, which had been converted to the ammonium salt, was dissolved in 1 ml. of water and added to 4 ml. of 0.19 *N* sulfurous acid (0.6% as SO_2) in a Pyrex tube (10 ml. volume) which was sealed and heated at 160–170° for 30 min. (adapted from the method of Hayek and Shriner.[67] The reaction mixture was treated with phenylhydrazine hydrochloride and afforded a yellow, crystalline solid which was recrystallized twice from aqueous pyridine, m.p. 194–200° dec., unchanged on addition of authentic D-*arabino*-hexose phenylosazone of m.p. 200–202° dec. The osazone was converted to the osotriazole by the method of Hann and Hudson[68]; m.p. 194–196°, unchanged on admixture with authentic D-*arabino*-hexose phenylosotriazole of m.p. 194–195°.

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(62) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, *ibid.*, **67**, 527 (1945); M. L. Wolfrom, A. Thompson, T. T. Galkowski and E. J. Quinn, *Anal. Chem.*, **24**, 1670 (1952).

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(64) G. B. Robbins and F. W. Upson, *ibid.*, **60**, 1788 (1938); **62**, 1074 (1940).

(65) This adsorbent was prepared as follows. A solution of 1 liter of concd. hydrochloric acid, sp. gr. 1.1878, in 3 liters of water was prepared and 1 kg. of Magnesol was added to the solution with good agitation. After stirring for 1 hr., the suspension was diluted with 4 liters of water and stirred briefly before allowing to settle. The supernatant liquid was removed by siphoning, 2 liters of water was added, the suspension was stirred briefly and allowed to settle again. After repeating this treatment 6 to 8 times, a slurry of the precipitate was poured into an 8 liter percolator and washed without suction with distilled water (about 60 liters) until only a trace of chloride ion could be detected in the last washings. Finally the product was washed with 3 liters of acetone and dried in the percolator with suction. Final drying was accomplished in an oven at 110° for 12–18 hr. After screening to pass 200 mesh, the product was mixed with Celite 535 (Johns-Manville Co., New York, N. Y.) in a ratio of 5:1 by weight. Further drying at 160–180° increased the activity.

(66) R. C. Hockett and C. W. Maynard, Jr., THIS JOURNAL, **61**, 2111 (1939); V. Deulofeu, *J. Chem. Soc.*, 2602 (1930).

(67) M. Hayek and R. L. Shriner, *Ind. Eng. Chem.*, **36**, 1001 (1944).

(68) R. M. Hann and C. S. Hudson, THIS JOURNAL, **66**, 735 (1944).

Isolation of Glyoxal Bis-(2,4-dinitrophenylhydrazone).—The method of Grangaard, Gladding and Purves[24] was utilized on product II (200 mg.). This involves the formation of the bis-(dimethyl acetal) of glyoxal in methanol containing hydrogen chloride, steam distillation from a basic aqueous solution, hydrolysis with acid and precipitation as glyoxal bis-(2,4-dinitrophenylhydrazone); yield 7 mg., m.p. 315–320° dec. Product III (180 mg.) afforded 60 mg. of the derivative, m.p. 317–322° dec. Both samples had m.p. 318–325° dec. on admixture with authentic glyoxal bis-(2,4-dinitrophenylhydrazone) of m.p. 325–327° dec.[69]

Isolation of D-Glucitol Hexaacetate.—Product III (7.0 g.) was reduced with Raney nickel and hydrogen (2000 p.s.i.) in aqueous solution at 100° for 12 hr. After removal of the catalyst by filtration, the solution was made 0.6 *N* in sulfuric acid and heated at 100° for 24 hr. The acid was neutralized with barium hydroxide and the solution filtered. The residue obtained on evaporation of the filtrate was acetylated with acetic anhydride and fused zinc chloride at 50°. The reaction mixture was added to an ice and water mixture and the acid was neutralized with sodium bicarbonate. The aqueous solution was extracted with chloroform and the extracts were evaporated to a sirup; yield 5.8 g.

Chromatography of this sirup (1.9 g.) on Magnesol–Celite (column, 75 × 250 mm.) using 900 ml. of benzene/*t*-butyl alcohol 400/1 as the developer, afforded 0.2 g. of crystalline material (from the third zone from the top) after recrystallization from 75% ethanol, m.p. 98–99°, $[\alpha]^{21}D$ +10.7° (*c* 4, chloroform). The melting point was unchanged on admixture with authentic D-glucitol hexaacetate of m.p. 98.5–99.0° and $[\alpha]^{25}D$ +10° (*c* 4.6, chloroform).

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(69) H. H. Strain, THIS JOURNAL, **57**, 758 (1935).

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Preparations of the Synthetic Estrogens. VII.[1] New Syntheses of 1,1,2-Tri-*p*-anisyl-2-chloroethylene

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Treatment of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) with phosphorus pentachloride effected simultaneous chlorination and dehydrochlorination giving 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV). The required *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) was obtained by the condensation of *p*-anisylglyoxal or N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III) with anisole in the presence of concentrated sulfuric acid as a catalyst. *p*-Methoxy-α,α-di-*p*-anisylacetophenone (I) was reduced to corresponding carbinol V which was dehydrated to 1,1,2-tri-*p*-anisylethylene (VI). The tri-*p*-anisylethylene (VI) was also prepared by dehydration of 1,1,2-tri-*p*-anisylethanol (VII) which was obtained in good yield by means of a Grignard reaction between α-chloro-*p*-methoxyacetophenone and *p*-anisylmagnesium bromide.

In the previous paper[1] a new preparation of triarylbromoethylenes was described, in which the use of the Grignard reaction was avoided throughout the synthesis. An attempted adaptation of the method to the synthesis of triarylchloroethylenes resulted, however, in failure. Since some of such chloro derivatives are known to be not only active as estrogens but also effective in the treatment of prostatic cancer, investigation of new methods suitable for a large scale preparation has now been extended to these compounds. It was discovered that the treatment of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) with phosphorus pentachloride gave 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) in a 43% yield.

The required intermediate, *p*-methoxy-α,α,-di-*p*-anisylacetophenone (I), was prepared by the condensation of *p*-anisylglyoxal with anisole in the presence of sulfuric acid. *p*-Anisylglyoxal[3] was obtained by the oxidation of *p*-methoxyacetophenone with selenium dioxide. The condensation product I, however, formed a yellow viscous oil, which could not be crystallized,[4] and gave very poor yields of 1,1,2-tri-*p*-anisyl-2-chloroethylene (IV) upon treatment with phosphorus pentachloride. In an attempt to improve the yield, it was found that the condensed acetophenone derivative I could be obtained in a pure, crystalline form, when anisole reacted with *p*-anisylglyoxal prepared from N,N-dimethylaminophenyl-α-*p*-anisoylnitrone (III). The nitrone was obtained by the condensation of *p*-methoxyphenacylpyridinium bromide (II)[5] with *p*-nitrosodimethylaniline in the presence of 1 *N* sodium hydroxide solution according to the method of Kröhnke.[6] When this nitrone III was dissolved in an excess of anisole, hydrolyzed with 65% sulfuric acid to *p*-anisylglyoxal and treated with 98% sulfuric acid, *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) separated as crystals, m.p. 82–83°, in a 89% yield based on the nitrone III.[7]

$$p\text{-}CH_3O\text{—}C_6H_4COCHO + 2C_6H_5OCH_3 \xrightarrow{\text{concd. } H_2SO_4} p\text{-}CH_3O\text{—}C_6H_4COCH(C_6H_4\text{—}OCH_3\text{-}p)_2$$

I

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(2) Ben May Laboratory for Cancer Research, University of Chicago, until January, 1956.

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(5) E. Bamberger, *Ber.*, **20**, 3338 (1887).

(6) F. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

(7) For the condensation between phenylglyoxal and anisole see an abstract of a paper read before a meeting: K. Sisido and H. Nozaki, *Repts. Inst. Chem. Research, Kyôto Univ.*, **17**, 136 (1949); *C. A.*, **46**, 3032b (1952). α,α-Di-*p*-anisylacetophenone was reported in this abstract to form a yellow viscous oil, b.p. 267–273° (6 mm.), which could not be crystallized. Phenylglyoxal used was prepared by the oxidation of acetophenone with selenium dioxide according to the method of H. A. Riley and A. R. Gray ("Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509). In view of the experiences in the present synthesis of *p*-methoxy-α,α-di-*p*-anisylacetophenone (I) the condensation reaction was re-examined using phenylglyoxal hydrate prepared from N,N-dimethylaminophenyl-α-benzoylnitrone. The α,α-di-*p*-anisylacetophenone thus obtained formed colorless crystals, m.p. 91–92°, the details being described in the Experimental part. An attempted condensation of N,N-dimethylaminophenyl-α-benzoylnitrone with anisole in the same way as the *p*-anisoylnitrone (III) failed to afford the desired α,α-di-*p*-anisylacetophenone, giving a resinous product.