an iodine flask containing 10 ml. potassium iodide solution (5%). The solution was titrated with 0.01*N* sodium thiosulfate solution.

The values of X (% absorption of bromine) were plotted against time. From the resultant curves, as illustrated in Figure 1a, values of k_2 were calculated in (l.) (g.-mole)$^{-1}$ (min.)$^{-1}$. The results for the homogeneous reactions are reproducible.

B. *Addition of chlorine. Reagent.* Chlorine gas was dissolved in glacial acetic acid to prepare the solutions of required concentrations. Besides glacial acetic acid, three other aqueous acetic acid solutions were used: 10% water, 20% water and 40% water in acetic acid. Allyl chloride, 3,3-dichloropropene, and 3,3,3-trichloropropene were the same materials used for the bromine addition; 1,1,3-trichloropropene (b.p. 132°, 760 mm.), *cis*-1,3-dichloropropene (b.p. 104°, 760 mm.), *trans*-1,3-dichloropropene (b.p. 112°, 760 mm.), and vinyl bromide (b.p. 16°, 760 mm.) also were used in this experiment.

Procedure. Most of the procedure is identical with that of bromine addition, except that a special correction had to be made for the slight evaporation of chlorine.

The following sets of experiments were performed with different concentrations of acetic acid solutions. They could not be done at one concentration because of the great variation of rate. This procedure is valid provided a known value for one compound is available for each set of experimental conditions. Thus in Table II the relative rates for vinyl bromide and *cis*-dichloroethylene were known. The relative values obtained for *trans*-1,3-dichloropropene and 3,3,3-trichloropropene in the aqueous acetic acid with 20% water were in turn used as known values for comparisons made in solutions with 10% and 40% water in the acetic acid. It was found that the more dilute the acetic acid solution, the faster the rate for the less reactive allylic chlorides.

(a) In glacial acetic acid: (1) 3,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) Vinyl bromide (*M*/10), Chlorine (*M*/80).

(b) In aqueous acetic acid solution (10% water): (1) *cis*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) *trans*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80).

(c) In aqueous acetic acid solution (20% water): (1) *trans*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) 3,3,3-Trichloropropene (*M*/10), Chlorine (*M*/80).

(d) In aqueous acetic acid solution (40% water): (1) 3,3,3-Trichloropropene (*M*/10), Chlorine (*M*/80). (2) 1,1,3-Trichloropropene (*M*/10), Chlorine (*M*/80).

The values of X (% absorption of chlorine) were plotted against time as illustrated in Figure 1b and the rate k_2 evaluated from the slope (see Table I).

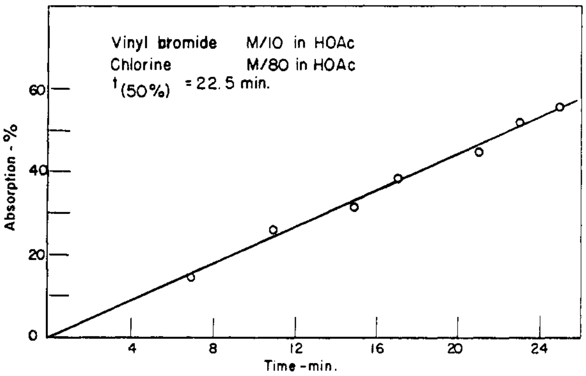

Fig. 1b. Chlorine addition to vinyl bromide

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CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, THE HEBREW UNIVERSITY]

On the Nitration of D-Fructose. I.

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Fructose was nitrated by nitronium sulfate. Six compounds were isolated, either as nitrate esters or—after denitration—as derivatives of fructose, four of which could be identified as dimeric condensation compounds of fructose anhydrides. Three of them are described: difructose-anhydride I, diheterolevulosan I, and diheterolevulosan II. A suggestion is put forward on the mechanism of their formation.

In their effort to identify possible decomposition products of cellulose nitrate[1] a large number of simple and compound sugars have been nitrated by Will and Lenze,[2] using nitronium sulfate as nitrating agent. Most of the sugars yielded the expected fully nitrated products, with the exception of xylose, glucose, fructose, and sucrose. From the monosaccharides crystalline nitrates of the anhydrides of the corresponding sugar could be obtained, besides some amorphous nitration products of ill-defined character. Complete nitration of xylose, glucose, and sucrose has been performed in more refined ways;[3–5] however, no success in full nitration of fructose has been reported.

This sugar differs from the others in its behavior towards strong mineral acids, the action of which causes dehydration and dimerization.[6] The properties of six difructose dianhydrides were summarized by Wolfrom *et al.*[7] The existence of monomeric

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[1] W. Will, *Ber.*, **24**, 400 (1891).

[2] W. Will and F. Lenze, *Ber.*, **31**, 68 (1898).

[3] L. Brissaud, *Mem. services chim. état*, **30**, 120 (1943).

[4] G. Fleury and L. Brissaud, *Compt. rend.*, **222**, 1051 (1946).

[5] E. J. Hoffmann and V. P. Hawse, *J. Am. Chem. Soc.*, **41**, 235 (1919).

[6] A. Pictet and J. Chavan, *Helv. Chim. Acta*, **9**, 809 (1926).

[7] M. L. Wolfrom, W. W. Binkley, and H. W. Hilton, *J. Am. Chem. Soc.*, **74**, 2867 (1952).

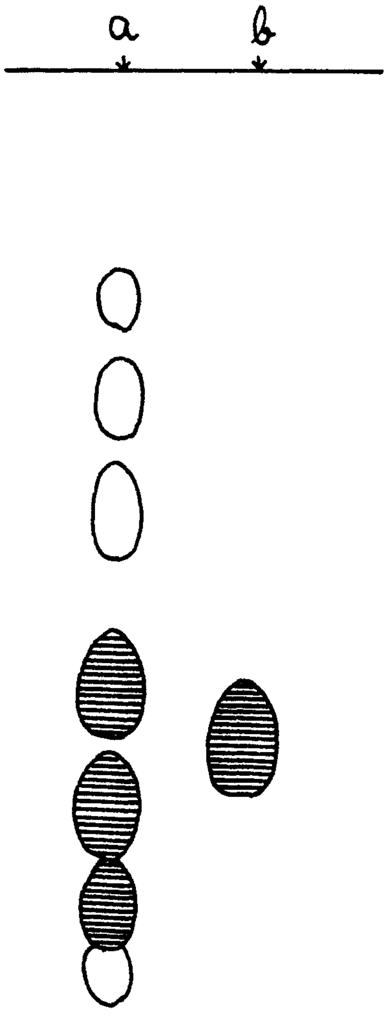

Fig. 1. a. Reduction products of the noncrystalline fraction (III) obtained by nitration of fructose. b. D-Fructose

fructose anhydrides has been reported several times[6,8] and a suggestion put forward that these compounds dimerize rapidly. The only well defined monomeric fructose anhydride was prepared by Sarel and Leibowitz[9] by nitration under nonacid conditions.

The purpose of the present work is to reinvestigate the nitration products of fructose as described by Will and Lenze.[2]

By the action of nitronium sulfate on fructose a dextrorotatory amorphous powder (I) was obtained which could be separated into an ethanol soluble fraction (II) and an insoluble sirup (III). From II and III two crystalline compounds separated (IV and V), both proving to be nonreducing hexanitrates of a difructose dianhydride. IV and V differed markedly in their x-ray diffraction pattern, but had similar positive rotatory power and the same analytical composition and infrared absorption spectra. On catalytic reduction they were both converted into the same substance (VIII), identified as "Difructose Anhydride I". Renitration of VIII yielded IV again. IV and V are therefore one substance, exhibiting dimorphism; they are apparently the "α-fructosan trinitrate" described by Will and Lenze,[2] but they constitute a small fraction only of I. No other homogeneous fructose derivative could be isolated from I by fractionation from different solvents or by chromatography which produced but a minute quantity of another crystalline substance (VI) which proved to be nitrogen-free and is presumably an oxidation product of fructose (*meso*-tartaric acid?).

Compound III was subjected to catalytic hydrogenolysis,[10] using low hydrogen pressure. The dextrorotatory crude reduction product (VII) reduced Fehling's solution rapidly and was developed by paper chromatography into 7 spots, none of which is identical with fructose (Fig. 1). Six crystalline compounds could be obtained by column chromatography, three of which were identified with well defined fructose derivatives, namely "Difructose Anhydride I" (VIII), "Diheterolevulosan I" (IX), and "Diheterolevulosan II" (X). A fourth substance (XI) falls into a new class of nonreducing compound carbohydrates, consisting of fructose and methylglyoxal; this substance will be described elsewhere. The remaining two crystalline compounds (XII, XIII) show exceptionally high values of optical rotatory power.

The nature of the products isolated so far reveals that the action of nitronium sulfate on fructose results in esterification, polymerization, dehydration, anhydride formation, oxidation, and cleavage of the C—C bonds.

The complete absence of fructose from VII (Fig. 1) seemed rather surprising, since this sugar is kept in the acidic nitration medium for not more than 20–30 minutes. Most of this period is necessary for sufficient separation of the products from the reaction mixture. By using a technique for extracting the crude nitration product which further minimizes the contact between the product and the reactants, a levorotatory product (XV) was obtained. Its reduction product (XVI) could be resolved by paper chromatography into four strong and seven faint spots, predominant among them a spot identical with fructose (Fig. 2).

Thus, the initial formation of a nitrate of monomeric fructose has been demonstrated. This result could be confirmed by chromatographic analyses of the denitration products derived from the crude nitrates which have been prepared from fructose in the absence of sulfuric acid, according to the methods of Brissaud[3] (XVII) and Oldham[11] (XIX). In both cases the fructose spot was prominent in the paper chromatogram (Fig. 2).

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(8) L. Sattler and F. W. Zerban, *Sugar,* **39,** No. 12, 28 (1944).

(9) M. Sarel and J. Leibowitz, *J. Org. Chem.,* **24,** 141 (1959).

(10) L. P. Kuhn, *Anal. Chem.,* **20,** 276 (1950).

(11) J. W. H. Oldham, *J. Chem. Soc.,* **127,** 2840 (1925).

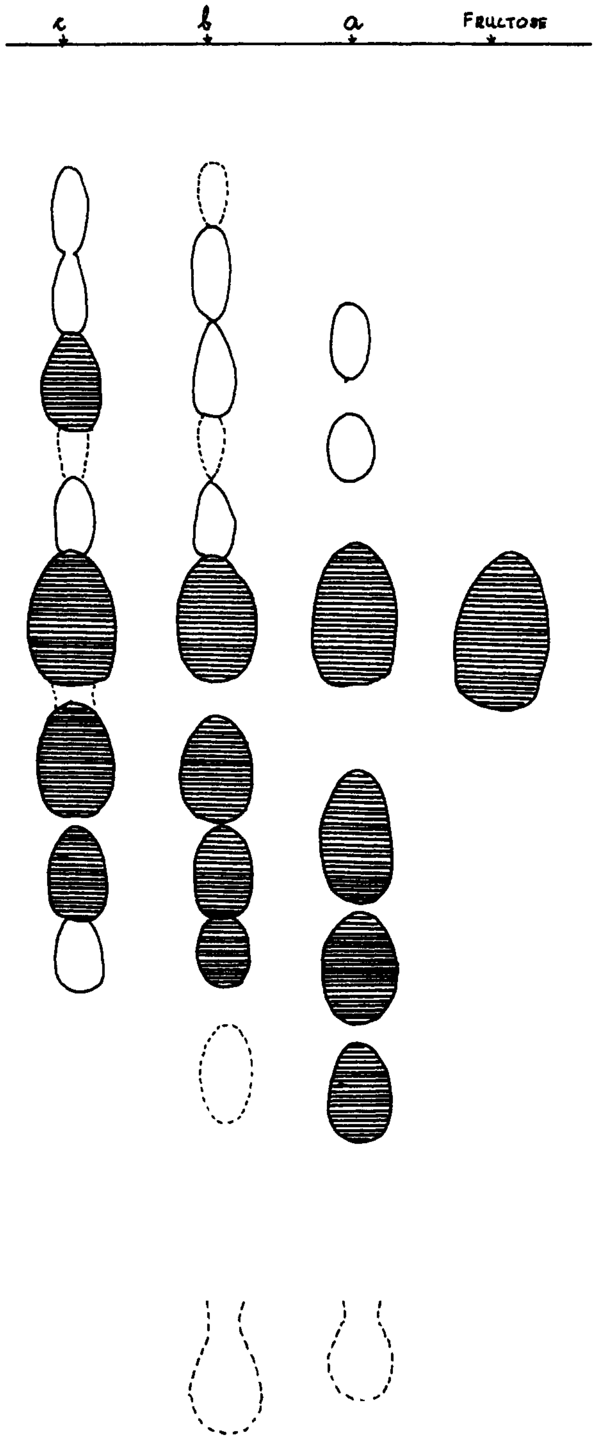

Fig. 2. a. D-Fructose nitrated by an HNO$_3$-P$_2$O$_5$ mixture and reduced. b. D-Fructose nitrated by HNO$_3$-H$_2$SO$_4$ (method B) and reduced. c. D-Fructose nitrated by an HNO$_3$-AcOH-Ac$_2$O mixture and reduced

The formation of difructose dianhydrides by dry[12] or concentrated aqueous hydrochloric acid[6] never exceeded 50%, although the time of reaction might last several days. After acid treatment of inulin Jackson and Goergen[13] were able to isolate difructose dianhydrides but could not obtain them from D-fructose treated in a similar manner.

Difructose anhydride I was formed by the action of concentrated nitric acid on inulin acetate.[14]

In our experiments it has been shown that nitrates of fructose are formed initially but that these subsequently undergo anhydridization and dimerization. It can be presumed that tetra- and penta-nitrates of fructose exceed free fructose in their reactivity. Nitrate groups on C-1, C-2, and C-3 would differ considerably in the mechanism of the fission of their C—O—NO$_2$ linkages. The removal of an —ONO$_2$ group from C-2 of fructose might produce anhydro derivatives with or without Walden inversion; both these possibilities have been realized in the case of the hydrolysis of β-acetonitro glucose.[15] The formation of a monomeric anhydride from (XVII), as β-2,3-*anhydro*-fructofuranose (XXI) of Sarel and Leibowitz, demands a free hydroxyl group on C-3 as it exists in D-fructose 1,2,4,6-tetranitrate. This incomplete nitration takes place only when the introduction of the nitrate group is performed by dinitrogen pentoxide or nitric acid in acetic anhydride, while the nitronium ion in a strong acid medium effects complete esterification. Fructose, nitrated by nitronium sulfate and reduced, yielded only traces of XXI, and no XXI was found after the action of nitric acid in presence of phosphorus pentoxide.

The spontaneous decomposition of penta- or 1,3,-4,6-tetra-nitrate of fructofuranose can be compared to the action of nitric acid on triacetyl inulin.[14] The free ketolic OH on C-2 might acquire acidic properties by the influence of the neighboring nitrate-oxygen atom on C-1 of a neighboring molecule. This mechanism implies the liberation of nitric acid (or nitrous gases) from the nitrate esters–a phenomenon which in fact could be observed.

However, the large variety of products obtained by the action of acids on fructose indicates the co-existence of several reaction mechanisms. In a strongly acidic medium C-2 undoubtedly serves as potential carbonium ion,[16] thus facilitating the formation of an unstable epoxy-ring after elimination of nitric acid (Fig. 3a) or alternatively, the formation of a more stable anhydric bond with some C—O—NO$_2$ group of a second molecule, also with the elimination of HNO$_3$. In case this reaction is performed with the C-1-ONO$_2$ group—which seems most probable—the conditions for the formation of a dioxan-like structure are realized, as the second molecule is able to react in a similar way with the first one (Fig. 3b). Less probable is the formation of an anhydride involving C—3—ONO$_2$ (Fig. 3c), although a compound of this type

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(12) H. H. Schlubach and C. Behre, *Ann.*, **508**, 16 (1933).

(13) R. F. Jackson and S. Goergen, *Bur. Standards J. Research*, **3**, 27 (1929).

(14) J. C. Irvine and J. W. Stevenson, *J. Am. Chem. Soc.*, **51**, 2197 (1929).

(15) E. K. Gladding and C. B. Purves, *J. Am. Chem. Soc.*, **66**, 76 (1944).

(16) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

Probable mechanisms of anhydride formation in a strong acid medium

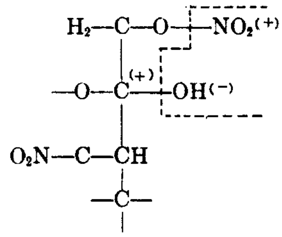

Fig. 3a

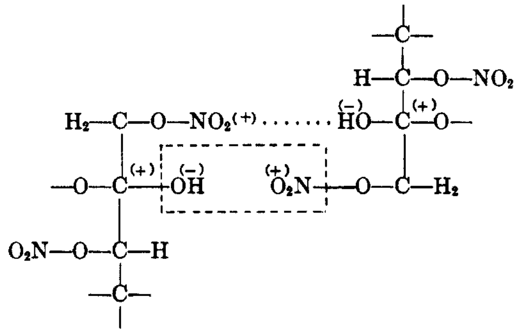

Fig. 3b

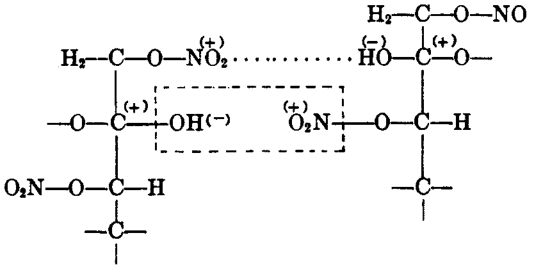

Fig. 3c

has been isolated.[17] Any other type of anhydric bond which did not result in a dioxan-like structure, would be unstable and probably undergo fission under the conditions of the reaction.

Moreover, the nitrated products undergo more easily a C—C fission which produces three-carbon-derivatives, as will be shown in a subsequent paper.

EXPERIMENTAL

Reagents. Absolute nitric acid (d_{15} 1.52) was prepared by vacuum distillation[18] of a mixture consisting of 1 part of nitric acid 70% and two parts of sulfuric acid 98% (v./v.) at temperatures not exceeding 20° (0.4 mm. Hg), and the distillate was collected in liquid air. *D-Fructose* (N.B.C.) was ground and sieved (mesh 100 and up) and dried over phosphorus pentoxide to constant weight. Dry *ethanol,* used for crystallizations, was prepared from commercial absolute ethanol by means of magnesium and iodine.[19] *Acetic acid and acetic anhydride* were freshly distilled before use. *Chloroform* was cleaned by means of aqueous sulfuric acid and washed with water until neutral, dried over calcium chloride, and distilled. *Nitrobenzene* was washed with water, dried over anhydrous soda and lyophillized at 2 × 10^{-2} mm. Hg.

Catalytic hydrogenolysis was carried out in a Parr apparatus at a hydrogen pressure of 60 lb./sq. inch (approx. 4 atm.), using twice as much palladium catalyst,[10] 10% on charcoal, as nitrates. After 20 min. the reactions with diphenylamine and Nessler's reagent were negative.

Quantitative chromatographic separations were carried out by means of a column containing a mixture of Florex-Celite (Hiflo)[20] 5:1, using 200 g. of the adsorbent for each gram of the carbohydrate mixture.[7]

Paper chromatographic separations (descending) were performed on Whatman No. 1 filter paper (for chromatography). If not stated otherwise, the developing mixture consisted of 9 parts butanol, 8 parts water, and 5 parts pyridine. Each separation was run in duplicate, using for spot detection resorcinol 0.25% in phosphoric acid (85%), diluted 1:10 by ethanol in one case, and anthrone reagent in the other case. The location of the spots was copied with a soft lead pencil as described by Sattler and Zerban.[21]

Analyses. Nitrogen determinations were carried out according to Kuck *et al.*,[22] using either a solution of the nitrate ester in 96% ethanol or dry material in a tiny aluminum cup, which dissolved completely within 1 min. X-ray powder diffraction diagrams were photographed with a Guinier-De Wolfe camera (dispersion constant 4 mm./degree) with Cuα K radiation.[23] Infrared absorption spectrography was carried out on a Baird IR Spectrophotometer Model B, using a sodium chloride prism. Carbon/hydrogen determinations were carried out by Drs. G. Weiler and F. B. Strauss, G. B. Oxford. Melting points were determined by a Fisher-Jones apparatus and are uncorrected.

Procedures. Nitration of D-fructose by nitronium sulfate (Method A).[2] Thirty grams of D-fructose was dissolved in 300 ml. abs. nitric acid at 10° by addition in small portions (2–3 min.) and 600 ml. of sulfuric acid (precooled to 5°) was added with constant stirring over a period of 15–20 min., keeping the temperature of the reaction mixture at 15–18°. Soon turbidity set in and a sirup was formed. After all the acid was added, the mixture was transferred to a separating funnel and the sirup allowed to separate (15–30 min.). The turbid acid mixture was removed and the sirup allowed to run into a large mortar containing crushed ice, whereupon it turned into a white solid. This was thoroughly ground, the water-ice layer decanted and fresh ice added. After 15–20 repetitions of this procedure the ice water was neutral towards litmus. The solid was then dried by suction and then kept overnight *in vacuo* over P_2O_5 at 5°. In this way 32–35 g. of the crude product (I) was obtained, $[\alpha]_D^{22}$ +11° (ethanol).

Anal. Found: N, 12.9.

Separation of the trinitrates: (a) I was partly dissolved by shaking mechanically for 4 hr. with 50 ml. of abs. ethanol, yielding a colorless solution (II) and a yellowish sirup (III). II was kept at room temperature for two weeks during which fine needles (IV) separated. By recrystallization from absolute ethanol large monoclinic rods were obtained, $[\alpha]_D^{28}$ +49.5° (abs. ethanol, *c* 1.9), $[\alpha]_D^{27}$ +49° (*c* 8.6 in absolute methanol), $[\alpha]_D^{25}$ +37.7° (*c* 6.1 in benzene).

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(17) M. L. Wolfrom and M. G. Blair, *J. Am. Chem. Soc.*, 70, 2406 (1948).

(18) An airbalasted "Speedivac" rotatory pump, single stage model 1SC30, Edwards & Co. Ltd., London, was used.

(19) A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green & Co. Ltd., London, 1951, p. 166.

(20) Florex XXX, a fuller's earth type produced by the Floridin Company, Warren, Pa. Celite (Hiflo) a silicious filter-aid produced by Johns Manville Company, New York, N. Y.

(21) L. Sattler and F. W. Zerban, *Ind. Eng. Chem.*, **41**, 1401 (1949).

(22) J. A. Kuck, A. Kingsley, D. Kinsey, F. Sheeham, and G. F. Swigert, *Anal. Chem.*, **22**, 604 (1950).

(23) The authors are indebted to Prof. A. Alexander and Dr. Z. Kalman of the Department of Physics of the Hebrew University, for carrying out these measurements.

Anal. Calcd. for $C_6H_7N_3O_{11}$: C, 24.24; H, 2.32; N, 14.14. Found: C, 24.5; H, 2.66; N, 14.1.

Melting point was 140° with a distinct transformation at 125°. At this latter temperature the transparent needles turn spontaneously opaque, but show no sign of melting until the temperature of 140° is reached. This transformation does not cause any change in weight or rotatory power: after recrystallization of the opaque substance from ethanol, IV is regained quantitatively.

(b) When the mother liquor of IV was concentrated by slow evaporation over a course of several weeks at room temperature, it turned slowly into a thin sirup from which small tetrahedric crystals (V) separated. The thin sirup was diluted with some cold ethanol and V was removed rapidly by decantation and filtration. Further small quantities of V were obtained after slurrying III with sufficient cold ethanol and could be separated by filtration. After treatment with cold abs. ethanol V remained in the form of small prismatic spheres, m.p. 138°, $[\alpha]_D^{25}$ +47.6° (*c* 1.47 in methanol).

Anal. Calcd. for $C_6H_7N_3O_{11}$: C, 24.24; H, 2.32; N, 14.14. Found: C, 24.15; H, 2.45.

V showed the same transformation at 124–125° as IV. When V was dissolved in warm methanol or ethanol and the solution cooled, a mixture of IV and V resulted; upon repetition of this, V was completely converted into IV. No complete reconversion of IV into V was successful; however some V was formed when a hot abs. ethanolic solution of IV was slowly concentrated by a stream of dry air.

IV and V rapidly decomposed when heated with camphor or benzophenone and were only slightly soluble in cold benzene. Molecular weight determinations were carried out in colorless nitrobenzene: 0.4602 g. (IV) in 18.10 g. (15 ml.) nitrobenzene—ΔT = 0.31°; mol. wt. = 575. 0.4602 g. (IV) in 24.19 g. (20 ml.) nitrobenzene—ΔT = 0.23°; mol. wt. = 580. 0.0427 g. (V) in 3.65 g. (3 ml.) nitrobenzene ΔT = 0.14°; mol. wt. = 586. 0.0427 g. (V) in 6.10 g. (5 ml.) nitrobenzene ΔT = 0.08°; mol. wt. = 608. $C_6H_7O_2(NO_3)_3$ theor. mol. wt. = 594.

Both IV and V showed identical infrared absorption bands at 1665 cm.$^{-1}$; 1306 cm.$^{-1}$; 1280 cm.$^{-1}$, characteristic for nitrate esters. X-ray powder diffraction data of IV: 5.05 (1 = strongest); 4.70 (4); 4.00 (2); 3.80 (5); 3.65 (3).

X-ray powder diffraction data of V: 8.40 (3); 5.55 (4); 5.05 (7); 4.65 (8); 4.30 (1); 3.80 (2); 3.55 (5); 2.85 (6). V might well contain some amount of IV.

From the sirupy concentrate of II minute amounts of cubic crystals (VI), m.p. 138°, separated after several weeks. VI was free of nitrogen, optically inactive, and did not reduce Fehling's solution. It dissolves in alkaline solution.

Anal. Found: C, 29.87; H, 3.02.

VI might well be impure mesotartaric acid (m.p. 140°, C, 32.0; H, 3.0), but its quantity was insufficient for recrystallization.

Catalytic reduction of IV *and* V. Compound IV (0.089 g.) was dissolved in 4 ml. of dioxan and diluted with 6 ml. of 95% ethanol. One-tenth gram of palladium catalyst, 10% on charcoal, was added and this mixture shaken under hydrogen pressure of 1360 lb./sq. inch for 10 min. The filtrate of the resulting mixture gave no reaction with diphenylamine, Nessler's reagent, or Fehling's reagent. A white sirup (0.053 g.) could be isolated (97.5%) and from its abs. ethanol solution small crystalline aggregates were formed (VIII); $[\alpha]_D^{22}$ +27.5° (*c* 3.8 in water), m.p. 164–165° (uncorr.).

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.22. Found: C, 44.26; H, 6.59.

Compound V (0.239 g.) was reduced as described above, forming 0.120 g. (88%) of a colorless sirup. After treatment with abs. ethanol, crystals identical with VIII appeared.

Acetylation of (VIII). Compound VIII (376 mg.) was dissolved in 2.0 g. of acetic anhydride and 0.4 g. sodium acetate added. The mixture was heated to 140° for 30 min. and then kept for 40 hr. at 70°. On cooling to room temperature and neutralization, a jelly-like precipitate was formed that was extracted by 3 × 20 ml. of chloroform. After evaporation of the solvent a sirup remained, containing some acetic acid that was removed by distillation with toluene. The sirup was taken up in some ether and crystallized by addition of benzene, yielding 470 mg. (70%) of the hexaacetate of difructose anhydride I. $[\alpha]_D^{18}$ +0.56° (*c* 8.89 in chloroform); m.p. 138°. This hexaacetate showed a transformation at 126–127°, similar to the transformation observed with IV and V, *i.e.*, its long transparent needle-like crystals turned spontaneously opaque with no signs of melting. This hexaacetate (55 mg.) was subjected to deacetylation by a methanolic solution of barium methoxide. After shaking the mixture for 4 hr. at room temperature, it was neutralized by *N* sulfuric acid in methanol over a period of 5 hr., the resulting suspension filtered with a filter aid and concentrated *in vacuo*. Recrystallization from abs. ethanol yielded 34.5 mg. (77% theor.) of (VIII).

Nitration of VIII. Compound VIII (30.8 mg.) was dissolved in 2 ml. of a mixture containing abs. nitric acid, acetic acid, and acetic anhydride at a ratio of 2:1:1 (w./w.), all freshly distilled.[8] A white precipitate was formed that was introduced into 30 ml. ice water. By centrifugation a yellowish jelly-like aggregate separated; this was washed with ice water until neutral, filtered, and air-dried. One-tenth gram of decolorizing carbon (Norit A) was added to its alcoholic solution, filtered off, and the clear solution concentrated until a jelly-like precipitate appeared. This was redissolved by gentle heating and inoculated with IV. Overnight a nearly quantitative yield of crystalline IV was obtained. These crystals melted at 140°, but showed their transformation at 107° instead of 125°.

Experiments with III. When an ethanolic solution of III was kept at −5° for several weeks, small spherical aggregates appeared which did not reduce Fehlings solution. Their optical activity varied between −5° and +20° and their nitrogen content between 13% and 14.6%. The homogeneity of these fractions was checked by reduction, followed by paper chromatography. All of them proved to be complex mixtures of 3 or 5 components. Unsuccessful fractionations were attempted from various solvents and solvent mixtures, including aqueous and dry methanol, acetone, dioxane, ethyl acetate, petrol ether, chloroform, carbon tetrachloride, ether, benzene, nitrobenzene, pyridine, and acetic acid.

When III was subject to low-pressure hydrogenolysis a sirup (VII) was formed reducing Fehling's solution rapidly, $[\alpha]_D^{17}$ +5°. By paper chromatography of VII, using a mixture of 25 parts of ethyl acetate, 8 parts of water, and 7 parts pyridine, six spots appeared after color reaction with resorcinol, anthrone, and α-naphthol. In relation to R_f of fructose = 1.00, the average distances travelled by these (R_f) spots were as follows: 0.32; 0.63; 0.84; 1.27; 1.34; 1.57. Owing to the diffuse character of the slower spots, further paper chromatographic separations were carried out with a mixture of butanol, water, and pyridine. Seven spots could be located after color reaction with resorcinol, their R_f values being as follows: (a) 0.35; (b) 0.50; (c) 0.67; (d) 0.92; (e) 1.12; (f) 1.25; (g) 1.35 (see Fig. 1). Three of these spots could be identified with well-defined compounds, namely: (a) diheterolevulosan I (di-D-fructopyranose 1,2′; 2,1′-dianhydride); (c) diheterolevulosan II (D-fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride); (e) difructose anhydride I (di-D-fructofuranose 1,2′:2,1′-dianhydride).

Quantitative chromatography of III. Five grams III were dissolved in 10 ml. of water, diluted by 190 ml. methanol and added to a column containing 1000 g. of a mixture of Florex XXX–celite (Hiflo) 5.1[7] (dimensions 310 × 90 mm.) prewetted by 1500 ml. ethanol 95%. The chromatogram was developed by 2500 ml. methanol 95%, followed by 2000 ml. of methanol 90%, 1000 ml. methanol 75% and 1000 ml. methanol 50%. The effluents were collected in portions of 25 ml. and their optical rotations measured in a 4 dm. polarimetric tube. In this way the effluents could be divided into six fractions, each of which was shown by paper chromatography to contain 3–4 constituents.

These fractions, designated A (fastest moving), B, C, D, E, and F, were dried thoroughly *in vacuo* over phosphorus pentoxide. By addition of some dry ethanol to the horny residues, five crystalline substances were separated from A, B, C, and D at room temperature over a period of 10 weeks. From A and B small platelets (XI) could be isolated, which proved to be a condensation product of fructose and methylglyoxal, as will be described elsewhere; from the combined mother liquors diheterolevulosan I (IX) separated followed by small amounts of diheterolevulosan II (X). From C and D tiny amounts of strongly hygroscopic needles (XII) crystallized, $[\alpha]_D^{18}$ +270° (*c* 0.13 in methanol), m.p. 160° (dec.). So far the substance has not been obtained free from impurities. From D, E, and F some traces of small crystals (XIII) separated, $[\alpha]_D^{18}$ approx. −300° (*c* 0.10 in water). The amounts isolated were insufficient to permit purification and elementary analysis.

Nitration of D*-fructose by nitronium sulfate* (Method B): Three grams of D-fructose was dissolved with rapid stirring in 30 ml. of abs. nitric acid at 5° and this temperature kept during the entire procedure; 60 ml. of cold concentrated sulfuric acid was added over a period of 5 min., followed by 100 ml. of dry chloroform. After 2 min. of stirring, the upper chloroform layer was siphoned off, 50 ml. of fresh chloroform was added and the mixture was stirred for 2 min. This procedure was repeated once more and the combined chloroform extracts were repeatedly washed with 300 ml. portions of ice-cooled distilled water, until the aqueous layer was neutral towards litmus. After the first three washings, the chloroform layer was rapidly removed from the aqueous phase disregarding turbidity. To the almost colorless chloroform solution, 0.38 g. of recrystallized *p*-benzoquinone was added. The solution was dried for 4 hr. over anhydrous sodium sulfate and then concentrated *in vacuo* at 30°. There resulted 3.0 g. of a pale yellow sirup (XV) $[\alpha]_D^{18}$ −35° (*c* 2.0 in dioxan) (N = 13.1), which was dissolved in 15 ml. of dioxan, 20 ml. 95% ethanol were added, and the solution was reduced with 10 g. of palladium catalyst. After reduction a yellow sirup was obtained (XVI) that was subjected to paper chromatography (see Fig. 2).

Nitration of D*-fructose in an acetic anhydride mixture.*[3] Three grams of D-fructose was dissolved with rapid stirring in a mixture of 20 ml. abs. nitric acid, 15 ml. acetic acid, and 15 ml. acetic anhydride. The solution rapidly turned yellowish-brown; after 10 min. it was poured into 500 ml. of ice water. The product was extracted by three portions of 100 ml. ether, the combined yellow extracts were washed repeatedly with ice-cooled distilled water until neutral towards litmus. The ethereal solution was dried for 4 hr. over anhydrous sodium sulfate, 0.05 g. *p*-benzoquinone were added, and the ether distilled off. 5.70 g. of a deep yellow sirup (XVII) was obtained, $[\alpha]_D^{16}$ +30 (*c* 7 in methanol), N = 16. By hydrogenolysis of XVII a reddish-brown sirup was formed (XVIII). XVIII was subjected to paper chromatography (see Fig. 2).

Nitration of D*-fructose in presence of phosphorus pentoxide.*[11] Three grams of D-fructose was added to an ice-cooled mixture of 30 ml. abs. nitric acid, 30 ml. of dry chloroform and 6 g. of phosphorus pentoxide. After 5 min. of rapid stirring, 50 ml. of dry chloroform was added and the liquid part of the mixture siphoned off, leaving the phosphorus pentoxide in the reaction flask. The acid mixture was poured into 300 ml. of ice water, and shaken with an additional amount of 100 ml. of chloroform. The chloroform layer was removed and the turbid aqueous layer extracted twice with 100 ml. of ether. The mixed extracts were washed with ice-cooled distilled water until neutral, dried over anhydrous sodium sulfate, 0.02 g. of *p*-benzoquinone were added and the solvents evaporated *in vacuo*. 1.15 g. of an orange colored sirup (XIX) resulted, $[\alpha]_D^{17}$ −3.9°, N = 11.4. The reduction product (XX) of (XIX) was subjected to paper chromatography (see Fig. 2).

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[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING DIVISION OF THE MIDWEST RESEARCH INSTITUTE]

The Phenylation and Methylation of Alkoxychlorosilanes[1]

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The phenylation of diisopropoxydichlorosilane, triisopropoxychlorosilane, and triethoxychlorosilane with chlorobenzene and molten sodium was investigated. The effect of varying the reactant ratio on the yield of diphenyldiisopropoxysilane from the reaction of diisopropoxydichlorosilane, chlorobenzene, and molten sodium was studied. The methylation of triethoxychlorosilane and triisopropoxychlorosilane with methyl chloride and molten sodium was studied briefly. During this investigation, four new isopropoxychlorosilanes were prepared and characterized: diisopropoxydichlorosilane, triisopropoxychlorosilane, phenylisopropoxydichlorosilane, and phenyldiisopropoxychlorosilane.

Various modifications of the sodium method of preparing organosilicon compounds have been devised to control the degree of substitution. One approach[3] is based upon limiting the concentration of the organic halide in the reaction mixture by extreme dilution with an inert solvent. A two-stage synthesis[4] in which the organosodium reagent is prepared and treated separately allows much better control. Another approach to controlled substitution is based on the relative reactivities of the silicon-alkoxy and silicon-chlorine bonds toward the organosodium intermediate.

One objective of this study was to determine the effect on the phenylation and methylation reactions due to varying the type of alkoxy groups in the silane starting material. Another objective was to determine the effect of varying the reactant ratio

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