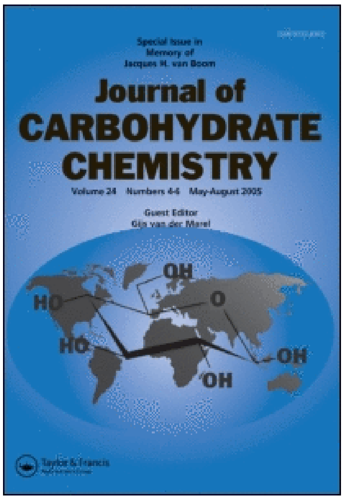

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Synthesis and Photolysis of Sugar Nitrates. Trifluoromethanesulfonate (Triflate) Displacement by the Nitrate Anion

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SYNTHESIS AND PHOTOLYSIS OF SUGAR NITRATES. TRIFLUOROMETHANESULFONATE (TRIFLATE) DISPLACEMENT BY THE NITRATE ANION.[1]

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ABSTRACT

1,2:3,4-Di-O-isopropylidene-6-O-nitro-α-D-galactopyranose (13), 1,2:5,6-di-O-isopropylidene-3-O-nitro-α-D-glucofuranose (14), 2,3:4,5-di-O-isopropylidene-1-O-nitro-β-D-fructopyranose (15), methyl 2,3-O-isopropylidene-5-O-nitro-α-D-ribofuranoside (16), and 1,2:5,6-di-O-isopropylidene-3-O-nitro-α-D-allofuranose (17) were synthesized by reacting the appropriate triflates (1, 5, 3, 4, and 2, respectively) with tetrabutylammonium nitrate in refluxing benzene. These compounds (13-17) and 1,2:4,5-di-O-isopropylidene-3-O-nitro-β-D-fructopyranose (19) also were prepared by reacting the appropriate alcohols (7, 11, 9, 10, 8, and 12, respectively) with fuming nitric acid in acetic anhydride. The nitrates 13-16 and 19 were photolyzed in 2-propanol to give the corresponding deprotected alcohols. Photolysis of the nitrate 17, however, gave the C_3 inverted alcohol 11. A mechanism is proposed for the deprotection and rearrangement of 17 upon irradiation.

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INTRODUCTION

The esterification of a carbohydrate with nitric acid produces a type of compound often referred to as a sugar nitrate (equation 1).[2] Several sugar nitrates are sufficiently useful that they have become commercially important compounds. For example, esterification of cellulose under the proper conditions produces a powerful explosive, cellulose nitrate. Fully esterified glycerol (glycerol trinitrate, also an explosive) lowers blood pressure and, consequently, can be used in the treatment of hypertension. In addition to these quite varied practical applications, nitric esters of carbohydrates are sometimes synthetically useful.

$$\mathrm{ROH} + \mathrm{HNO_3} \xrightarrow{\mathrm{CHCl_3}} \mathrm{RONO_2} + \mathrm{H_2O} \qquad (1)$$

In the laboratory, formation of sugar nitrates is used occasionally as a method for hydroxyl group protection. The value these esters have as protecting groups is that they are stable in the presence of acids and many of the reagents used in carbohydrate synthesis. There are disadvantages also. These esters are unstable in the presence of strong bases. Most methods for their formation (e.g., nitric acid in chloroform or acetic anhydride) use strongly acidic conditions. In addition, although deprotection normally occurs without difficulty, the two most effective methods for this process, catalytic hydrogenolysis and reaction with hydrazine (a powerful nucleophile) in refluxing ethanol, both are capable of causing changes in addition to deprotection (in some molecules).

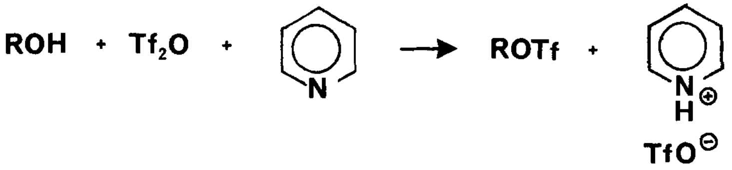
The purpose of the research described in this paper was two-fold. The first objective was to investigate a method for formation of sugar nitrates which depended upon displacement of the trifluoromethanesulfonate (triflate) leaving group. The second goal was to study a photochemical process for deprotection of carbohydrates protected as nitrate esters.

RESULTS AND DISCUSSION

A. SYNTHESIS OF SUGAR NITRATES BY TRIFLATE DISPLACEMENT

Nitrate esters can be synthesized by substitution reactions in which the nitrate anion functions as the nucleophile. This type of reaction is not particularly attractive, in general, because the nitrate anion is a relatively poor nucleophile and displacement of typical leaving groups (*e.g.*, tosylate and mesylate) is not uniformly successful. If, however, the leaving group is the unusually easily displaced triflate, the possibility exists for a considerable increase in the number of sugar nitrates being formed by displacement reactions. Since triflate displacement usually is an S_N2 process, a normal feature of this reaction is inversion of configuration at a chiral center. This feature is undesirable in some situations but can be advantageous in others. When the various advantages and disadvantages of nitrate ester synthesis by triflate displacement were combined, this type of reaction appeared to have sufficient promise to merit investigation.

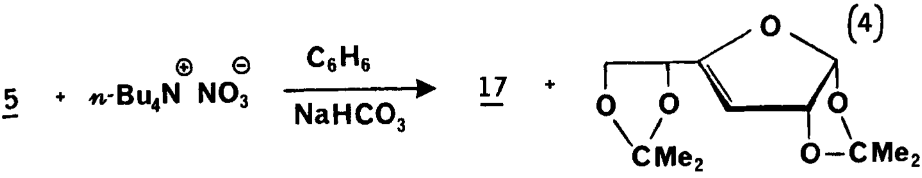
The triflates 1-6 were synthesized from the corresponding, partially protected carbohydrates 7-12 by reaction with triflic anhydride and pyridine in dichloromethane (equation 2). Each of these compounds (1-6) reacted with tetrabutylammonium nitrate in refluxing benzene; however, only compounds 1-5 produced



(2)

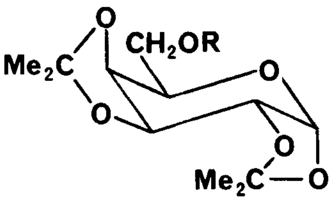
$$ROTf + Bu_4N^{\oplus} NO_3^{\ominus} \longrightarrow RONO_2 + Bu_4N^{\oplus} TfO^{\ominus} \quad (3)$$

(4)



18

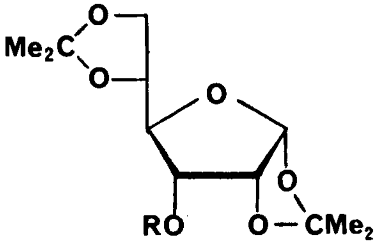
the expected nitrates 13-17 (equation 3). Also, although 1,2:5,6-di-O-isopropylidene-3-O-triflyl-α-D-glucofuranose (5) reacted with tetrabutylammonium nitrate to give the expected 1,2:5,6-di-O-isopropylidene-3-O-nitro-α-D-allofuranose (17), the unsaturated sugar 1,2:5,6-di-O-isopropylidene-α-D-ribo-hex-3-enofuranose (18) also was formed (equation 4). During formation of these compounds (17 and 18), the reaction mixture became decidedly acidic and considerable



1 R = Tf

7 R = H

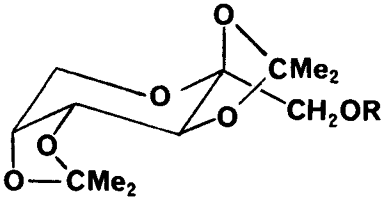
13 R = NO_2



2 R = Tf

8 R = H

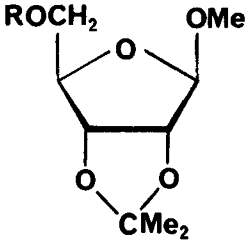
17 R = NO_2



3 R = Tf

9 R = H

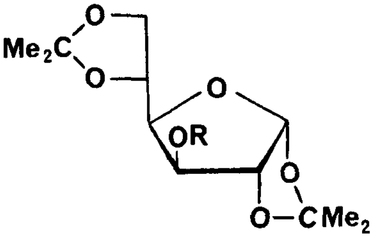
15 R = NO_2



4 R = Tf

10 R = H

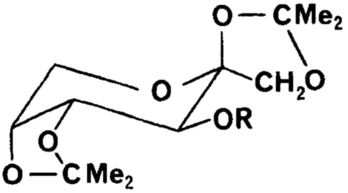
16 R = NO_2



5 R = Tf

11 R = H

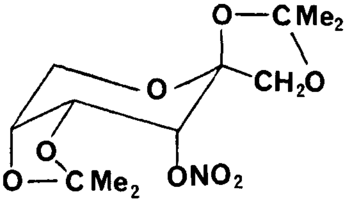
14 R = NO_2



6 = Tf

12 = H

19 = NO_2



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product decomposition was apparent. This decomposition was avoided by adding sodium bicarbonate to the reaction mixture prior to heating in order to immediately remove any acid generated in the elimination process.

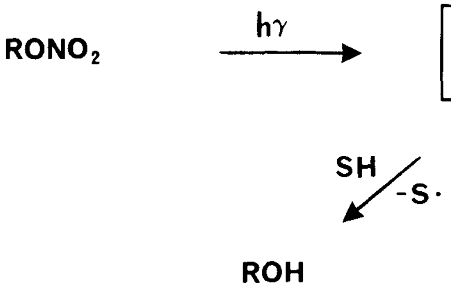
In contrast to the reaction of the triflates 1-5, reaction of 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose (6) with tetrabutylammonium nitrate *did not produce any of the expected* 1,2:4,5-*di*-O-isopropylidene-3-O-nitro-β-D-psicopyranose (20). Addition of sodium bicarbonate to the reaction mixture did not prevent the formation of a complex mixture of products in this case.

The nitrate esters 13-17 and 19 were synthesized independently in excellent yield by reaction of the appropriate alcohols (7, 11, 9, 10, 8, and 12, respectively) with nitric acid in acetic anhydride according to the method of Honeyman and Stening.[4] In comparison with the Honeyman method, triflate displacement appears to be a less general procedure for sugar nitrate synthesis; therefore, the value of triflate displacement as a hydroxyl protection reaction depends upon its application in special situations. One situation where triflate displacement could be useful is when simultaneous inversion of configuration at a particular chiral center and hydroxyl group protection are required. A second possible situation is when acid sensitive compounds are being reacted. These compounds should be stable during triflate formation and reaction.

B. PHOTOLYSIS OF SUGAR NITRATES

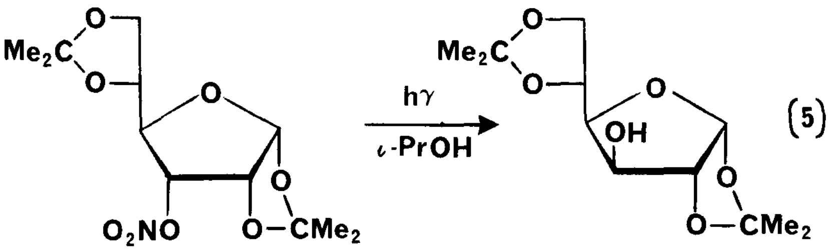
The available information on the photolysis of nitrate esters suggests that photochemical reaction is a possible deprotection process. Irradiation of these esters in non-carbohydrate systems is thought to produce alkoxy radicals;[5] thus, photolysis of sugar nitrates in the presence of hydrogen donors represents a potentially effective technique for their deprotection (Scheme 1).

Corex-filtered irradiation ($\lambda > 240$ nm) of the nitrates 13-16 and 19 in 2-propanol under nitrogen with a



SCHEME 1

450-W Hanovia, mercury-vapor lamp resulted in formation of the alcohols 7, 11, 9, 10, and 12, respectively. These reactions were essentially quantitative; no other products were formed. In contrast, irradiation of 17 under the same conditions gave exclusively the C_3 inverted alcohol 11 (equation 5). Therefore, although photochemical deprotection worked well in five instances, it is clear from the sixth reaction (equation 5) that care must be exercised in the use of this method. In order to better understand when the photochemical deprotection reaction can be conducted without rearrangement, a detailed study of the mechanism for conversion of 17 into 11 was undertaken.



(5)

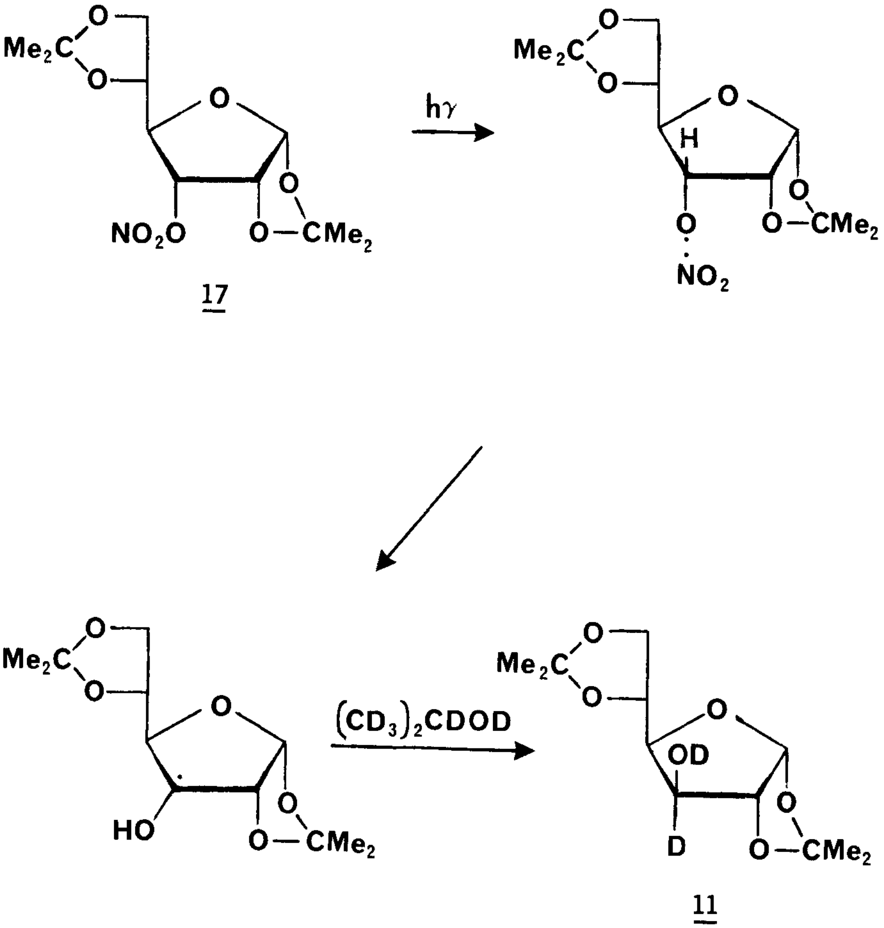
17 11

C. MECHANISTIC STUDY OF THE PHOTOCHEMICAL REACTION OF 1,2:5,6-DI-O-ISOPROPYLIDENE-3-O-NITRO-α-D-ALLOFURANOSE (17).

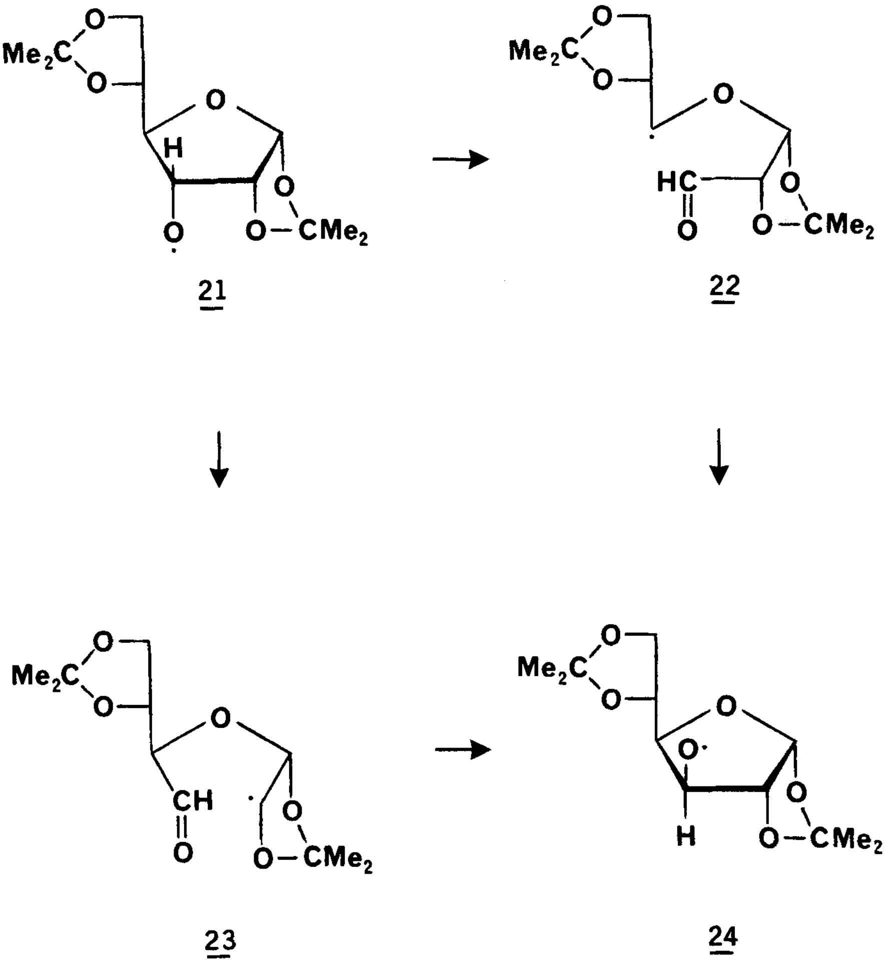
Since one of the four bonds to C_3 must have been broken during photolysis of 17, the possible fragmentation of each of these bonds needed to be considered. If the C_3-O bond were being broken during reaction, isomerization could occur by conversion of the nitrate ester 17 into its C_3 epimer 14 and then photolysis of 14 to give the observed product 11. The intermediacy of 14 was tested by irradiation of 17 to partial (27%) completion and analysis of the reaction mixture. Only unreacted starting material (17) and the rearranged alcohol 11 were present. Since compounds 14 and 17 have similar UV spectra and are consumed at comparable rates during photolysis, 14 should have been present in the reaction mixture if it were an intermediate in the formation of 11 (equation 6).

A second possibility for the inversion of configuration at C_3 during photolysis of 17 was that the C_3-H bond was broken and re-formed during reaction. This possibility was tested by photolysis of 17 in 2-propanol-d_8. If the C_3-H bond were being broken during reaction, the incorporation of deuterium into the product should result. (A proposed mechanism for such a reaction is given in Scheme 2.) Since no C_3 deuterium incorporation occurred, the C_3-H bond must have remained intact during photolysis.

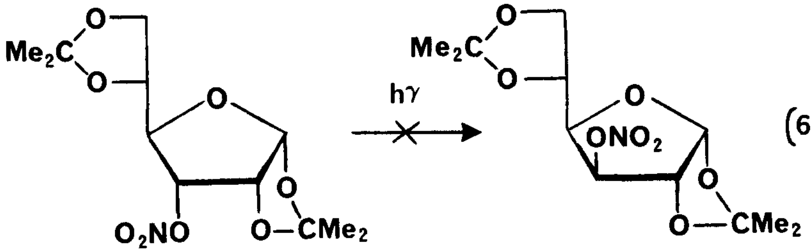
The results from the experiments just described pointed to an inversion of configuration at C_3 in compound 17 which began with a ring-opening of the alkoxy radical 21 to produce one of the intermediates 22 or 23 (Scheme 3). This opening then would be



SCHEME 2

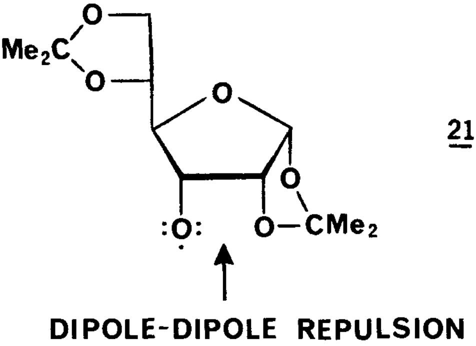


SCHEME 3



(6)

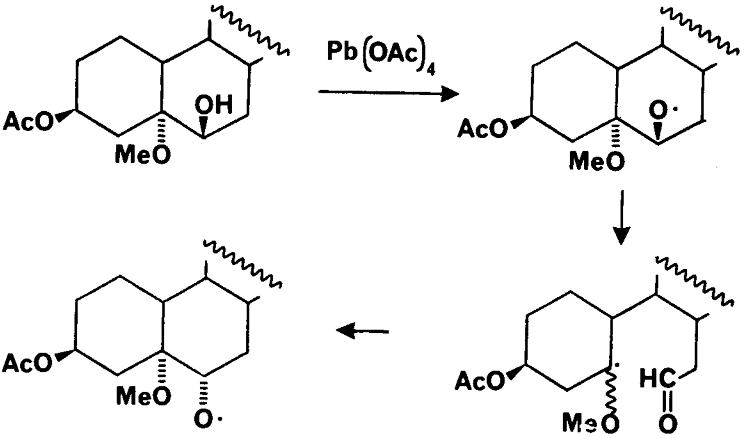
followed by ring-closure to give the epimeric alkoxy radical 24. Analogous reactions have been observed in non-carbohydrate systems (*e.g.*, Scheme 4).[6] Ring-opening of 21 would be expected to favor formation of 23 because the dipole-dipole repulsion between the C_2-O and C_3-O bonds should weaken the C_2-C_3 bond



21

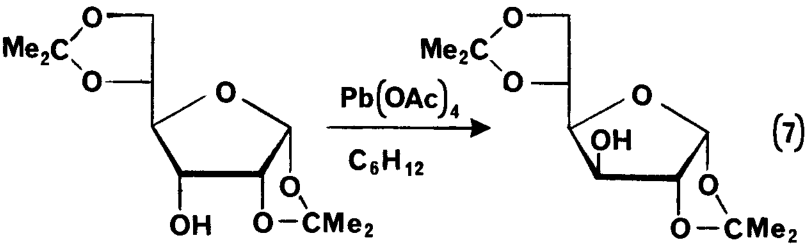
relative to the C_3-C_4 bond. Minimization of dipole-dipole interaction also would explain closure of 23 to give exclusively 24. A further observation favoring C_2-C_3 bond cleavage is that C_3-C_4 fragmentation would allow inversion of configuration at C_4. No C_4 inverted product was formed.

Although all available information was consistent with a ring-open intermediate in the rearrangement



SCHEME 4[6]

of 17 to 11, a more direct test of this proposed mechanism seemed desirable. This test consisted of attempting to generate the radical 21 by a non-photochemical process and observing its reaction. Reaction of alcohols with lead tetraacetate is a known method for generating alkoxy radicals.[7] When compound 8 was treated with lead tetraacetate in refluxing cyclohexane,[8] it rearranged quantitatively to 11 (equation 7).



8 11

Thus, the photochemical rearrangement of the nitrate ester 17 to the C_3 inverted alcohol 11 seemed to be best explained by the mechanism shown in Scheme 3. This type of rearrangement probably should be expected whenever significant dipole-dipole repulsion in an alkoxy radical can be relieved by ring-opening.

EXPERIMENTAL

General Procedures. ^{1}H NMR spectra were obtained ($CDCl_3$) from a Varian T-60 spectrometer and ^{13}C NMR spectra ($CDCl_3$) were determined using a Varian FT-80A spectrometer. All spectra are given in tabular form in Tables 1 and 2. Spectral simulation was done by using Varian Associates Simeq spin simulation program.

Synthesis of the Triflates 1-5. The triflates 1-5 were synthesized from the corresponding alcohols 7-11, respectively, by a procedure previously reported. This procedure is essentially the same as that given below for compound 6.

Synthesis of 1,2:4,5-Di-O-isopropylidene-3-O-triflyl-α-D-fructopyranose (6). 1,2:4,5-Di-O-isopropylidene-α-D-fructopyranose (6) (1.00 g, 3.84 mmol) and 1.30 mL of anhydrous pyridine were dissolved in 20 mL of CH_2Cl_2 in a round-bottom flask. This flask was fitted with an addition funnel containing 1.6 mL (9.6 mmol) of triflic anhydride in 10 mL of CH_2Cl_2. The system was closed, cooled to -20 °C (dry ice—CCl_4), and the triflic anhydride solution was added dropwise to the stirred reaction mixture. After 2 h, the solution was poured into 50 mL of rapidly stirred ice

Table 1. ^{1}H NMR Spectral Data[a]

H-1, H-1	H-2	H-3	H-4	H-5	H-6, H-6'	CH_3
4.49-3.87	—	4.75 $J_{3,4}$=6.9	4.49	—	3.87	1.50, 1.37,
5.43 $J_{1,2}$= 5.0	4.77-4.33	4.40	—	3.77	4.77-4.33	1.46, 1.30
5.79 $J_{1,2}$=3.5	4.55 $J_{2,3}$=0.0	5.47-5.23	4.30	—	3.70	1.48, 1.28
4.86, 4.38 $J_{1,1'}$=12.7	—	4.29 $J_{3,4}$=2.6	4.62 $J_{4,5}$=7.8	4.25 $J_{5,6}$=1.7 $J_{5,6'}$=1.0	3.90, 3.77 $J_{6,6'}$=13.0	1.52, 1.38,
4.97	4.77	4.50	4.57	4.33	—	1.30, 3.33
5.90 $J_{1,2}$=3.9	4.88 $J_{2,3}$=5.1	5.10 $J_{3,4}$=6.5	4.33	—	3.88	1.54, 1.35
4.04, 3.92 $J_{1,1'}$ =9.30	—	5.23 $J_{3,4}$=7.0	4.51	—	4.05	1.55, 1.42,

---

mical shifts are relative to Me_4Si (0 ppm). Coupling constants are in Hertz.
mical shifts for H-4, H-5, H-6, and H-6' and coupling constants $J_{4,5'}$ $J_{5,6'}$
6'', and $J_{6,6''}$ were obtained by spectral simulation.

TABLE 2. ^{13}C NMR Spectra Data[a]

Compound	6[b]	13	14	15	16[c]	17	19
C-1	71.5	96.3	105.1	71.7	109.8	104.7	71.8
C-2	102.4	71.0[d]	83.9[d]	100.8	85.1	79.5[d]	103.2
C-3	83.7	70.8[d]	82.4[d]	71.0[d]	82.5[d]	77.9[d]	79.0
C-4	74.2[d]	70.4[d]	79.3	70.8[d]	81.7[d]	77.5[d]	74.1[d]
C-5	74.2[d]	64.7	71.9	70.0[d]	72.9	75.1[d]	73.9[d]
C-6	60.2	71.7	67.4	61.5		66.0	60.5
$Me_2\underline{C}$	113.0	110.0	112.7	109.4	113.0	114.0	112.8
	110.2	110.0	109.8	109.3		110.3	110.1
$(\underline{C}H_3)_2C$	30.2	26.0	26.9	26.4	26.4	27.1	27.7
	27.5	26.0	26.6	25.8	24.9	26.5	26.4
	26.0	24.9	26.2	24.9		26.3	26.2
	25.5	24.4	25.1	24.0		24.8	25.9

a. Chemical Shifts are relative to Me_4Si (0 ppm).

b. There is an additional absorption at 118.0 ppm (J_{CF} = 320 HZ).

c. There is an additional absorption at 55.2 ppm (OCH_3).

d. Assignments may be interchanged.

water. The phases were separated and the aqueous phase was extracted with 50 mL of CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and the solvent distilled under reduced pressure. The residue was extracted with three 25 mL portions of hexane. The hexane was distilled under reduced pressure, first with a water aspirator and then with a mechanical pump, to give 1.5 g (3.8 mmol, 99% yield) of 1,2:4,5-di-O-isopropylidene-3-O-triflyl-β-D-fructopyranose (6) as a clear syrup. (^1H and ^{13}C NMR spectra of 6 are given in Tables 1 and 2, respectively.) This material began to turn color (red-brown) in a few h at room temperature and decomposed significantly after 24 h. It was stable for days at -20 °C.

Synthesis of the Nitrates 13-17 and 19. The nitrates 13-17 each were synthesized by two methods, triflate displacement and nitration with nitric acid in acetic anhydride. 1,2:4,5-Di-O-isopropylidene-3-O-nitro-β-D-fructopyranose[12] (19) was synthesized only by the latter method.

A. Nitrate Formation by Triflate Displacement (Typical Procedure). 2,3:4,5-Di-O-isopropylidene-1-O-triflyl-β-D-fructopyranose (3) (1.50 g, 3.82 mmol) and 2.30 g (7.55 mmol) of tetrabutylammonium nitrate were dissolved in 70 mL of benzene. The reaction mixture was refluxed for 25 h and the solvent was then distilled under reduced pressure to give a pale brown syrup. This material was extracted with three 50 mL portions of hot hexane. The combined extracts were filtered and the hexane was evaporated under reduced pressure to give 0.99 g (3.2 mmol, 85% yield) of a slightly yellow syrup. This material was homogeneous by TLC and crystallized on standing. It was recrystallized from hexane, mp 72-73 °C and identified as 2,3:4,5-di-O-isopropylidene-1-O-nitro-β-D-fructopyranose (15) on the basis of its ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) spectra and its elemental analysis. Anal. Calcd for $C_{12}H_{19}NO_8$: C, 47.21; H, 6.27; N, 4.59. Found: C, 47.46; H, 6.31; N, 4.42 Further confirmation of the structure of 15 (and the other carbohydrate nitrates) was obtained from its independent synthesis as described below in part B.

B. Nitrate Formation by Reaction With Nitric Acid in Acetic Anhydride. The procedure was essentially that reported by Honeyman and Stening.[4] 2,3:4,5-Di-O-isopropylidene-β-D-frucotpyranose[11] (3) (6.00 g, 23.1 mmol) was dissolved in 20 mL of acetic anhydride maintained at 0 °C. A mixture of red, fuming nitric acid (2.90 mL, 69.2 mmol) and 15 mL of acetic anhydride, also at 0 °C was added slowly to the rapidly stirred sugar solution. The reaction mixture was held at 0 °C for an additional 30 min and then poured into 100 mL of ice water and stirred for 5 min. The aqueous layer was decanted and the remaining yellow oil was stirred with 50 mL of saturated $NaHCO_3$. The aqueous layer was decanted and the residue was washed twice with ice water. During the washing process, the oil crystallized. This material was recrystallized from hexane to give 5.5 g (18.0 mmol, 78% yield) of the nitrate 15, mp 72-73 °C, identical with the material obtained from triflate displacement.

The ^{1}H and ^{13}C NMR spectra of the nitrates 13-17 and 19 are given in Tables 1 and 2. These compounds were homogeneous by TLC (silica gel, 1:9, ether-hexane). Product yields from triflate displacement and from the nitric acid reaction are given in Table 3. Compounds 13[4], 14[4], and 19[13] had been previously prepared and were identical to the materials described in the literature. The elemental analysis and mp for 15 are given above. Compound 16 was a syrup. Anal. Calcd for $C_9H_{15}NO_7$: C, 43.37; H, 6.07; N, 5.62. Found: C, 43.14; H, 5.93; N, 5.40. Compound 17 crystallized and was recrystallized from hexane. Anal. Calcd for $C_{12}H_{19}NO_8$: C, 47.21; H, 6.27; N, 4.59. Found: C, 46.99; H, 6.37; N, 4.61.

Reaction of 1,2:5,6-Di-O-isopropylidene-3-O-triflyl α-D-glucofuranose (2) With Tetrabutylammonium Nitrate. The reaction of the triflate 2 (1.50 g, 3.42 mmol), tetrabutylammonium nitrate (2.30 g, 7.55 mmol), and $NaHCO_3$ (1.0 g, 11.9 mmol) was conducted as described in the general procedure. TLC analysis of the reaction

TABLE 3. Product Yields From Preparation of Nitrates 13-17 and 19.

Compound	Percent Yield Triflate Displacement	Nitric Acid
13	93	69
14	50[a]	70
15	88	92
16	72	95
17	98	74
19	--	95

a. Compound 18 also formed in 50% yield.

mixture after "work-up" showed that it consisted of a mixture of two compounds. These were separated on a 2.5 x 10 cm column of silica gel (240-400 mesh) using 1:9 ether-hexane. The first 100 mL contained 0.41 g (1.7 mmol, 50% yield) of 1,2:5,6-di-O-isopropylidene-α-D-ribo-hex-3-enofuranose (18), identified by comparison of its NMR spectra with those of an authentic sample.[13] The second 100 mL contained 0.52 g (1.7 mmol, 50%) of 1,2:5,6-di-O-isopropylidene-3-O-nitro-α-D-allofuranose (17).

Reaction of 1,2:5,6-Di-O-isopropylidene-3-O-triflyl-β-D-fructopyranose (6) with Tetrabutylammonium Nitrate. The reaction between the triflate 6 and tetrabutylammonium nitrate was conducted as described in the general procedure for triflate displacement. TLC analysis of the reaction mixture indicated that it was complex; it was not analyzed further.

Reaction of 1,2:4,5-Di-O-isopropylidene-3-O-nitro-β-D-fructopyranose (19) With Hydrazine Hydrate. 1,2:4,5-Di-O-isopropylidene-3-O-nitro-β-D-fructopyranose (19) (1.13 g, 3.70 mmol) and 0.42 mL (7.4 mmol) of hydrazine hydrate were dissolved in 30 mL of ethanol and the solution refluxed for 1.5 h. The ethanol and water were distilled under reduced pressure and the residue dissolved in hot hexane. Distillation of the hexane left compound 12 (0.86 g, 3.3 mmol, 89%), identified by comparison of NMR spectra with a known sample.[11]

Photolysis of the Nitrates 13-17 and 19. The following procedure was used for the photolysis of compounds 13-17 and 19. (Compound 15 is used as an example.) 2,3:4,5-Di-O-isopropylidene-1-O-nitro-β-D-fructopyranose

(15) (1.00 g, 3.3 mmol) and 0.73 g (8.7 mmol) of $NaHCO_3$ were dissolved in 250 mL of 2-propanol and purged with nitrogen for one h. The nitrogen purge was continued during three h of irradiation using a Corex-filtered, 450-W Hanova, mercury-vapor lamp. After irradiation, the solvent was distilled to give a residue which solidified. The hexane soluble material was extracted to give 0.94 g (3.6 mmol, 97%) of 1,2:4,5-di-O-isopropylidene-β-D-fructopyranose (9).[12] Similar irradiation of compounds 13, 16, 17, and 19 gave the corresponding deprotected alcohols 7 (100%), 10 (96%), 11 (100%), and 12 (92%), respectively. Irradiation of 17 gave 11 (100%). These compounds were identical (^1H NMR) to independently obtained samples.

Photolysis of 1,2:5,6-Di-O-isopropylidene-3-O-nitro-α-D-allofuranose (17) in 2-Propanol-d_8. Compound 17 (0.10 g,.33 mmol) was dissolved in 5 mL of 2-propanol-d_8, purged with nitrogen for 10 min, and irradiated for 5 h using a Rayonet photochemical reactor equipped with 2537 Å lamps. After irradiation the solvent was distilled and the ^1H NMR spectrum of the residue showed that 11 had formed with no deuterium incorporation at C_3.

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