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SYNTHESIS AND PHOTOLYSIS OF PROTECTED D-HEX-2-ULOPYRANOSYL AZIDES

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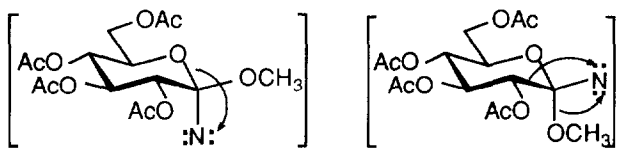
Abstract: Treatment of 3-*O*-methyl-1,2:4,5-di-*O*-methylethylidene-β-D-fructopyranose with trimethylsilyl azide in the presence of trimethylsilyl triflate in dry acetonitrile led, after neutralization and desilylation, to an anomeric mixture of 3-*O*-methyl-4,5-*O*-methylethylidene-D-fructopyranosyl azides in 94 % yield (α/β ~1/10). Likewise, 3-deoxy-4,5-*O*-methylethylidene-D-*erythro*-hex-2-ulopyranosyl azides were prepared from 3-deoxy-1,2:4,5-di-*O*-methylethylidene-β-D-*erythro*-hex-2-ulopyranose. The corresponding acetates and a mesylate were prepared in high yield under standard conditions. Photolysis of these azido sugars, in different solvents, led mainly to two labile, non-isolated imidates identified by NMR spectroscopy. For both α- and β-azides, the preferred cleavage of the C-2—C-3 bond and migration of the C-3 carbon to the nitrene led to the major ring-expanded photoproduct while migration of the C-1 carbon atom accounted for the structure of the minor *N*-substituted glycono-1,5-iminolactones formed. Migration of the ring oxygen atom was not observed, in keeping with other observations from the photolysis of cyclic and acyclic azido ethers.

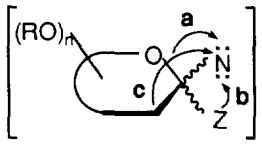
Amongst the variety of transformations involving the azido group, its photolytic or thermal decomposition is a long known process.[1] The intermediate nitrenes or nitrenoides[2] produced lead, as do carbenes, to 3 types of reactions: addition, insertion or 1,2-shifts.[3] While the first two pathways required favourable circumstances,[4] shift of an hydrogen atom attached to the nitrene-bearing carbon atom is a more general process resulting in imine formation. Several known syntheses of oxidized sugars took advantage of this propensity.[5-8] In the case of a nitrene attached to a quaternary carbon, 1,2-shifts of either alkyl or aryl groups have been observed while alkoxy groups appeared reluctant to undergo such shifts.[9] Hence, as concluded from photo- and thermolysis of acyclic α-azido ethers, the migratory ability of substituents decreases as follows:[9]

$$H >> CH_3 \geq Ph >> OR$$

However, our recent studies about the photolysis of either glycopyranosylidene diazides[10] or methyl 2,3,4,6-tetra-*O*-acetyl-1-azido-D-glucopyranosides[11] showed several examples of alkoxy group migration, resulting unexpectedly, in N—O bond formation. Not only these processes led to unprecedented ring-expanded structures by migration of the endocyclic O-5 oxygen atom, but they also revealed a hitherto unknown stereocontrol depicted below and demonstrated by the formation of a sugar-derived oxazepine derivative in yield as high as 70 % from tetraacetyl methyl (1*S*)-1-azido-β-D-glucopyranoside (axial azido group) whereas the same compound was formed in only 5 % yield from the α-anomer.[11] It is worth mentioning that the isolated compounds displaying such intracyclic N—O bonds are fairly stable, crystalline solids which were deacetylated uneventfully.



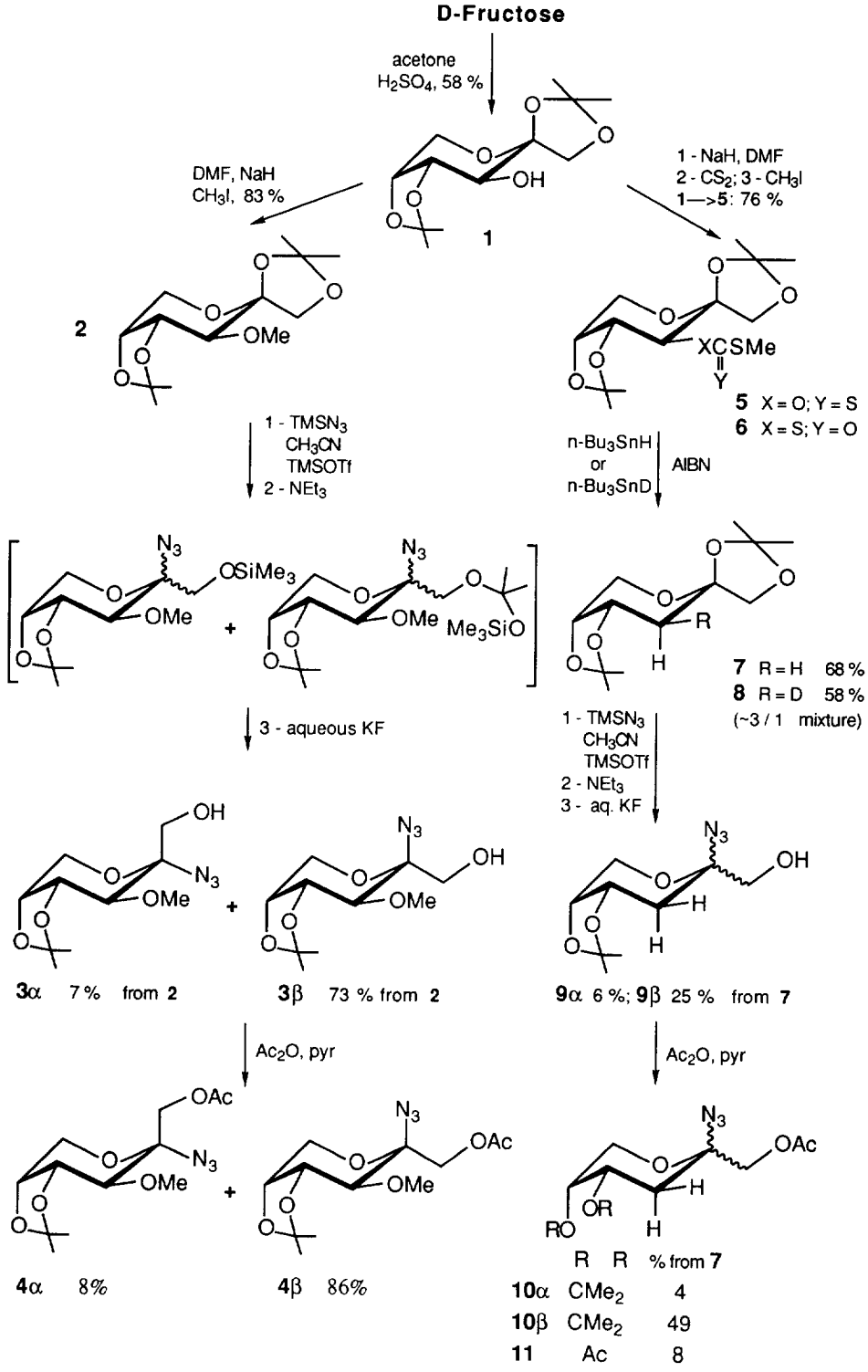
Hence, our results prompted us to extend our investigations concerning the photo/thermolysis of glycosyl azides[12] since these methods appeared incompletely explored as regard to either their synthetic potential[13,14] or the understanding of reaction pathways in connection with stereoelectronic effects[11] at the anomeric carbon. Other model compounds devoid of anomeric hydrogen atom were needed to get a closer insight in the possible ways (a, b or c) by which the reactive intermediates produced rearranged.



Since methyl 2,3,4,6-tetra-*O*-acetyl-1-azido-D-glucopyranosides required multistep syntheses, we turned out attention to ketoses. Interestingly, a recently published access to the herbicidal spirohydantoin (+)-Hydantocidin[15] described the preparation of psicofuranosyl azides by a Lewis acid-catalyzed opening of a 1,2-dioxolane and subsequent azidation at the anomeric carbon in the presence of trimethylsilyl azide. A related protocol was used for preparing β-D-fructopyranosyl fluorides.[16] Hence we decided to apply such an approach to the readily available 1,2:4,5-di-*O*-methylethylidene-β-D-fructopyranose[17] and to investigate the photolysis of the derived fructopyranosyl azides.

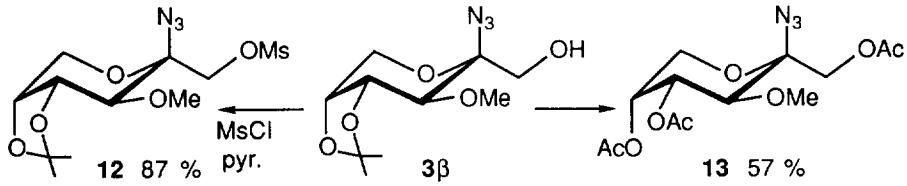
Powdered D-fructose was reacted with dry acetone under acidic, kinetic-controlled conditions to yield 1,2:4,5-di-*O*-methylethylidene-β-D-fructopyranose **1**.[17] To introduce a stable protecting group useful for NMR investigations, the latter was converted to the 3-*O*-methyl derivative **2**. When 3-*O*-methyl-1,2:4,5-di-*O*-methylethylidene-β-D-fructopyranose **2** in dry acetonitrile was treated with trimethylsilyl azide in the presence of a catalytic amount of trimethylsilyl triflate, the expected transformation[15] occurred. TLC monitoring of the reaction showed the formation of several more mobile compounds which corresponded to anomeric azides silylated[15] at either the initially attacked oxygen atom O-2 or the primary hydroxy group O-1, liberated by complete cleavage of the dioxolane moiety. After addition of triethylamine and on treatment with aqueous KF, these intermediates led to azides **3** (α/β : ~1/10) which were separated by column chromatography. Acetylation under standard conditions (Ac_2O, pyr) of an anomeric mixture of **3** afforded uneventfully the corresponding acetates **4** separable by column chromatography.

Since azidation of **2** proceeded satisfactorily, and in order to facilitate, hopefully, isolation and characterization of the photoproducts, we extended the aforementioned transformations to the 3-deoxy series. To this end, the thiomethylthiocarbonyl ester **5**[18] was prepared and deoxygenated in high yield following a literature procedure. Our observations confirmed that oxygen exclusion (argon atmosphere) was critical for the success of the deoxygenation step. In the case that this precaution was ignored or inappropriately secured, application of the Barton-McCombie reaction produced the desired 3-deoxy adduct in decreased yield (41 % instead of ~70-90 %[18]) accompanied


D-Fructose
acetone
H_2SO_4, 58 %
1
DMF, NaH
CH_3I, 83 %
2
1 - NaH, DMF
2 - CS_2; 3 - CH_3I
1—>5: 76 %
5 X = O; Y = S
6 X = S; Y = O
1 - $TMSN_3$
CH_3CN
TMSOTf
2 - NEt_3
n-Bu_3SnH
or
n-Bu_3SnD
AIBN
7 R = H 68 %
8 R = D 58 %
(~3 / 1 mixture)
3 - aqueous KF
1 - $TMSN_3$
CH_3CN
TMSOTf
2 - NEt_3
3 - aq. KF
3α 7 % from 2
3β 73 % from 2
9α 6 %; 9β 25 % from 7
Ac_2O, pyr
Ac_2O, pyr
4α 8%
4β 86%
R R % from 7
10α CMe_2 4
10β CMe_2 49
11 Ac 8

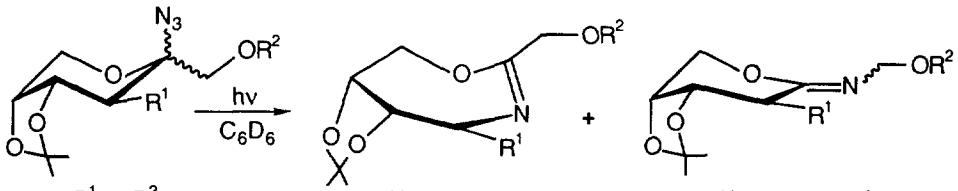
by unidentified byproducts and, interestingly, the transposed isomer **6** (12 %) resulting from a Freudenberg rearrangement.[19] It is worth mentioning that we also performed the Barton-McCombie deoxygenation in the presence of tributyltin deuteride. As judged from the ^{1}H NMR spectrum of the mixture, the isotopomer distribution was *ca.* 3/1 in favour of **8**. This ratio showed that the intermediate D-fructopyranos-3-yl radical was attacked preferentially from the β-side of the ring.

Azidation in the 3-deoxy series was carried out as above. Selective acid-catalyzed opening of the 1,2-methylethylidene group in the presence of $TMSN_3$ produced again a mixture of more mobile compounds only, as shown by TLC. However, after desilylation was completed, traces of polar products could be detected, thus explaining to some extent the lower yields recorded for **9**α and **9**β after an unoptimized separation by column chromatography. Even though **9**α gave a single spot on TLC plates, ^{1}H NMR spectroscopy showed the presence of an impurity which could result from hydrazoic acid elimination. Such 1,2-eliminations which are common in the 2-deoxy aldopyranosyl series,[20] most probably occurred again when a crude mixture of **9** was subjected to acetylation, since formation of the triacetylated byproduct **11** required the presence of an acidic species, other than acetic acid, during the last stage of the sequence. This assumption is supported by the fact that acetylation of 3αβ was highly selective as was the mesylation of 3β in pyridine to afford the corresponding mesylate **12** (87 %). Finally, acid-catalyzed hydrolysis of 3β followed by acetylation[21] led to 1,4,5-tri-*O*-acetyl-3-*O*-methyl-β-D-fructopyranosyl azide **13** in a 57 % yield.



Exposure to UV light effected the transformation of azides 3β, **4**, **9**, **10** (α and β), **12** and **13** within 2-3 h to give mainly two more polar products visible on TLC plates. For 4β, interposition of a filter was shown to result in an extended reaction time without selectivity improvement. In contrast to 3β which afforded a complex mixture [in which a 7-membered ring structure similar to **14** was present (**14**C, R^2 = H, ~10 %) as shown by the characteristic H-3 signal visible in the ^{1}H NMR spectrum as a deshielded dt], photolysis of 4β carried out in either C_6H_6, C_6D_6 or CD_3OD[22] led to mixtures of polar compounds containing mainly **14**A and **15**A, as shown by the yields calculated from the area of characteristic signals in the ^{1}H NMR spectra (H-1, H-1', H-3, OMe, OAc, methylethylidene): 74/7, 72/7.5, 56/13, respectively. Photolysis of the mesylate **12** in C_6D_6 led to a more complex mixture, possibly due to a longer reaction time (3.5 h), containing **14**B (~35 %) and **15**B (~6 %) as shown by ^{1}H and ^{13}C NMR. Similar rearrangements took place on photolysis of the α anomer 4α in C_6D_6. However, the composition of the crude reaction mixture (**14**A: 59 %, **15**A: 22 %) showed that the α anomeric configuration of the substrate was more favourable to imine formation: in this case, the ratio **14**A/**15**A was ~73/27 whereas the observations collected from other β-configurated azides led to ratio ranging from ~90/10 to 82/18. The unoptimized photolysis of 4β in CD_3CN and that of **13** in C_6D_6 led to mixtures in which the ring-

expanded structure **14**A and its tri-*O*-acetyl analogue could be identified by ^{1}H NMR as the major compound (65 and 35 %, respectively). Attempts to resolve structures **14**A and **15**A by column chromatography were unsuccessful, even when adding 1 % NEt_3 to the eluent. It is worth mentioning that flash-chromatography of **14**A and **15**A led to fractions that did not show any methoxy resonance in their ^{1}H NMR spectra whereas singlets corresponding to methyl groups (isopropylidene, acetate) were visible. Although a drawback, such a lability resulting in the initial loss of the methoxy group at C-3 supported, on the basis of the already observed lability of related ring-expanded adducts,[11] the structures deduced from NMR spectroscopy. Syntheses of azides **9** and **10** were carried out, in order to change the chemical nature of C-3 in the ring-expanded compound so as to prevent heterolysis at this centre. However, these efforts were not as rewarding as expected. In addition to the contamination of **9**α by an impurity, the complexity of ^{1}H NMR spectra of the crude photoproducts obtained from **9**α and **9**β hampered interpretation. This arose from the expected complex pattern of the sugar ring-protons and from the intrinsic lability of the *N,O*-hemiacetal branching in the 1,5-iminolactone produced from hydroxyazides **9**, likewise **15**C (R^2 = H) obtained from **3**β. Accordingly, the absence in the spectra of two deshielded doublets (from H-1 and H-1' in the corresponding D-*erythro* and D-*arabino*-pentono-1,5-iminolactones formed) was not surprising. Both ^{1}H NMR spectra recorded after photolysis of either **9**α or **9**β showed as the only well resolved signals two unidentified dd: δ 2.98 (J 12.8, J 2.0) and 2.44 (J 15.8, J 2.5), suggesting similar transformations of each anomer. The 3-deoxy azide **10**β led to, comparatively, less labile structures,[23] **16** and **17** in variable amounts depending on the irradiation time in C_6D_6 (2.25 h: **16**: ~50 %, **17**: 10 %, unchanged **10**β: 25 %; 4.5 h: **16**: ~50 %, **17**: none). Irradiation of **10**α in C_6D_6 for 3.25 h led to a mixture containing **16** (~50 %), besides unidentified products.



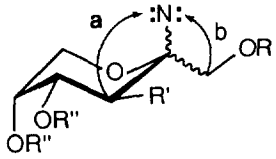
	R^1	R^2		% NMR		% NMR	ratio
4β	OMe	Ac	**14**A	72, 56[a]	**15**A	7.5, 13[a]	9 / 1, 8 / 2[a]
4α	OMe	Ac	**14**A	59	**15**A	22	73 / 27
12	OMe	Ms	**14**B	35	**15**B	6	85 / 15
10β	H	Ac	**16**	~50	**17**	10	83 / 17
10α	H	Ac	**16**	~50	**17**	b	b

[a] Photolysis carried out in CD_3OD, in the presence of $NaBH_3CN$ (3 eq); [b] not determined

Hence, contrary to expectations, all the evidence gathered pointed to the formation of compounds **14**A and **15**A from either **4**α or **4**β, or to analogues, from **10**α, **10**β, **12** and **13**. Whatever the anomeric configuration, protected D-fructopyranosyl azides led on photolysis to

reactive intermediates that rearranged essentially by cleavage of C—C bond between either C-2—C-3 (favoured) or C-1—C-2 and subsequent attachment of a carbon residue to the activated nitrogen atom. This showed that an axial orientation of the azido group in the substrate was not the clue essential for triggering N—O bond formation[11] in the intermediate nitrene since neither well-differentiated reaction pathways depending on the substrate anomeric configuration nor stable oxazepine derivatives could be observed in this study. In addition, these conclusions were similar to those arising from the photolysis of various 1-cyano-D-glycopyranosyl azides[24] which decomposed photolytically to form mainly ring-expanded structures, solved unambiguously by crystal analysis, again as a result of C—N bond formation. Hence, the observed preferential migrations of carbon residues towards nitrenes produced from D-hex-2-ulopyranosyl azides that can be considered as cyclic azidoethers, are in full agreement with the aforementioned investigations on acyclic azidoether photo and thermolysis.[9]

R = H, Ac, Ms
R' = H, OCH_3
R" = Ac, $C(CH_3)_2$



a : major pathway

Thorough spectroscopic investigations were needed to establish the anomeric configuration of the prepared D-hex-2-ulopyranosyl azides and the structure of the products obtained on photolysis. The first task could not be solved readily by NMR since ketopyranosyl derivatives are devoid of anomeric protons so that no valuable information, at least to this end, could be obtained from ^3J homonuclear couplings. However, since X-ray diffraction analyses have established unambiguously the structure of several crystalline D-fructopyranosyl derivatives[25,26] that showed, depending on their anomeric configuration, well-differentiated optical rotations, this last criterium appeared pertinent to ascertain the structure hypothesis based on chemical transformations. Hence, the anticipated β-anomeric configuration of the major D-*fructo*-and 3-deoxy-D-*erythro*-hex-2-ulopyranosyl azides prepared was confirmed by their optical rotations (**3**β: - 252, **4**β: - 205, **9**β: - 175, **10**β: - 124, **11**: - 165, **12**: - 139). Positive values were found for α anomers (**3**α: + 89, **4**α: + 43, **10**α: +90). The large ^3J couplings between H-3 and H-4 in compounds **5**, **6**, **11** and **13** indicated typical $^2C_5$ conformations whereas the smaller couplings observed for **7**, **9**β, **10**α and **10**β showed distorted pyranose rings.

For the sake of simplicity, parent sugar numbering will be retained along the discussion of the rearranged product structures. The ^1H and ^{13}C NMR spectra of the mixture obtained from **4**α and **4**β on photolysis could be fully interpreted. The H-3 resonance of the major compound **14**A appeared as a well-separated dt δ 5.01 ppm ($J_{3,4}$ 8.0 Hz) showing long range ^5J couplings with both H-1 and H-1' (two dd, $J_{3,1}$ 1.45, $J_{3,1'}$ 1.25 Hz) through the endocyclic C=N bond whereas the minor one **15**A exhibited two deshielded doublets at δ 5.78 and 5.63 assigned to H-1 and H-1'. Such deshielded doublets corresponded well to protons of a methylene carbon flanked by two heteroatoms. In addition, the sp^2-hybridization at C-2 in **15**A should induce a flattening of the

pyranoid ring which was shown by the small observed $J_{3,4}$ coupling (2.2 Hz) also found in glycono-1,5-lactones[27,28] and their *N*-substituted imino derivatives.[11,28,29] Moreover, the similarity of the chemical shifts recorded for the sp^2-hybridized carbon atoms of imidates **14**A and **15**A was expected [δ C-2: 151.4 (**14**A); 153.1 (**15**A)]. Structure **14**A was also supported by the 3.5 % enhancement of the H-3 signal, observed in nOe difference spectra, on irradiation of the methoxy protons at C-3, without affecting the remote H-1 and H-1' protons. This observation was not in favour of the 7-membered-ring isomer that might result from a N—O bond formation. Ring-expanded structures also formed predominantly on photolysis of **12** and **13** as shown by the presence of characteristic dt corresponding to the H-3 proton resonance in the ^{1}H NMR spectra. Similarly, the structure of the ring-expanded structure **16** obtained from **10**α and **10**β was deduced from the ^{1}H and ^{13}C NMR spectra which could be fully interpreted. For **16**, long-range couplings between H-1, H-1', H-3 and H-3' (~1 Hz) were observed[30] whereas, in the ^{13}C NMR spectrum, the C-3 methylene carbon atom appeared at lower field (46.7 ppm) as compared to the chemical shift observed for the same nucleus in **10**α (31.6 ppm) and **10**β (31.2 ppm), in keeping with the proposed structure. It is worth mentioning that the minor 1,5-iminolactone **17** obtained from **10**β also exhibited two deshielded doublets of doublets assigned to H-1 (δ 5.79, $J_{1,3e}$ 2.5, $J_{1,1'}$ 11.8 Hz) and H-1' (δ 5.62, $J_{1',3e}$ 2.1 Hz) as a result of an additional ^5J coupling with the H-3e proton through the exocyclic unsaturated C=N bond. Although **15** and **17** might exist as either the *E* and/or *Z* forms,[31] the collected NMR data were in favour of one stereoisomer only.[32] Similitude of $J_{3,4}$ couplings in **4**α, **4**β and **14**A were again compatible with the stereochemistry of the migrating carbon being retained.[10,11,24,33]

In conclusion, we prepared a series of protected D-fructopyranosyl azides as well as some 3-deoxy analogues. The key step of these syntheses consisted of an acid-catalyzed opening of a 1,2-methylethylidene group followed by nucleophilic attack of the anomeric carbocation to give predominantly β-configurated azides. Upon photolysis, these azides produced molecular nitrogen, *N*-substituted D-pentono-1,5-iminolactones (< 22 %) and ring-expanded imidates (< 74 %). The distribution and structures of the products led to the conclusion that the intermediate nitrenes rearranged by cleavage of bonds between either C-1—C-2 (minor pathway) or C-2—C-3 (preferred pathway), followed by attachment of carbon residues to the excited nitrogen atom. The resulting imidates were found to be labile so that structure determination relied on NMR spectroscopy. In that respect, the observed ^5J long-range homonuclear couplings through the either *endo* or *exo* cyclic C=N bond, the similar chemical shifts of the sp^2-hybridyzed C-2 carbon atom in **14** and **15** (A and B) and the deshielding of C-3 in **16** were of particular significance. Hence, ring-enlargement represented the major reaction pathway triggered by photolytic decomposition, whatever the anomeric configuration of the hex-2-ulopyranosyl azides studied. This conclusion is in complete agreement with those from other studies on photolysis of either cyclic or acyclic azidoethers. All the gathered evidence points to the fact that additional factors should be considered to explain the course of the reaction in the case of azidoacetals. A refined interpretation of this particular case will be proposed soon.

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EXPERIMENTAL:

General methods. Dichloromethane, acetonitrile and DMF were distilled over CaH_2. All the solvents used were distilled but commercially available reagents were used as purchased. For chromatography techniques, silica gel from Merck was used, either for column (Silica Gel Geduran Si 60) or plates (Silica Gel 60 F_{254}) which were exposed to H_2SO_4 spray followed by charring. Melting points, measured with a Büchi capillary apparatus, were not corrected. Optical rotations were determined with a Perkin-Elmer 241 polarimeter while infra-red spectra were obtained from a Perkin-Elmer 681 spectrophotometer. NMR spectra were recorded with Bruker AC 200/AM 300 spectrometers. Chemical shifts are expressed in ppm, using Me_4Si as the internal reference.

3-O-Methyl-4,5-O-methylethylidene-α- and -β-D-fructopyranosyl azides **3**α and **3**β. A mixture of trimethylsilyl azide (4.0 mL) and acetonitrile (2 mL) was added under stirring to an acetonitrile solution (40 mL) cooled to 0 °C and containing 3-*O*-methyl-1,2:4,5-di-*O*-methylethylidene-β-D-fructopyranose (2.75 g, 10 mmol). Then, trimethylsilyl triflate (0.51 mL, 3 mmol) diluted with acetonitrile (5 mL) was added dropwise. After 30 min, temperature was allowed to rise to ambient while stirring was maintained. TLC monitoring (ethyl acetate-hexanes 3:7 v/v) showed complete transformation of the starting material **2** (R_f 0.57) after 1h to give silylated intermediates visible on the TLC plates as more mobile spots (R_f 0.7 to 0.75). After the reaction was quenched by addition of triethylamine (0.8 mL), an aqueous solution (5 mL) of potassium fluoride (1.75 g) was added. Stirring was maintained for several hours whereupon TLC plates showed two more polar compounds. After the organic phase was concentrated under vacuum and the residue extracted with diethyl ether (3 x 30 mL), the combined organic phases were washed with brine (2 x 20 mL), then dried (Na_2SO_4) and concentrated to an oil. Resolution of the mixture was achieved by column chromatography to give first **3**β (1.89 g, 73 %) then **3**α (166 mg, 6.5 %).

3α: syrup, R_f 0.25 (ethyl acetate-hexanes 3:7 v/v); $[\alpha]_D$ +89° (c = 0.8, acetone, 20 °C); IR: ν N_3: 2100 cm^{-1}; ^1H NMR (DMSO-6d, 300 MHz) 5.22 (t, 1H, $J_{OH,H-1}$ 6.4, $J_{OH,H-1'}$ 5.6, O<u>H</u>), 4.29 (dq, 1H, $J_{5,6}$ 4.7, H-5), 4.23 (t, 1H, $J_{4,5}$ 6.5, H-4), 3.96 (dd, 1H, $J_{6,6'}$ 12.7, H-6'), 3.84 (dd, 1H, $J_{5,6'}$ 4.2, H-6), 3.68 (dd, 1H, H-1'), 3.52 (dd, 1H, $J_{1,1'}$ 12.1, H-1), 3.43 (s, 3H, OMe), 3.29 (d, 1H, $J_{3,4}$ 6.4, H-4), 1.44, 1.29 (2s, 6H, methylethylidene); ^{13}C NMR ($CDCl_3$) 64.2, 63.0 (C-1, C-6), 92.3 (C-2), 83.0, 71.3, 75.7 (C-3 to C-5), 60.4 (OMe), 110.2, 27.1, 24.9 (methylethylidene).

Anal.: Calcd. for $C_{10}H_{17}O_5N_3$: C, 46.33; H, 6.61; O, 30.86; N, 16.21; found: C, 46.17; H, 6.73; O, 31.26; N, 15.96.

3β: white solid, mp: 63 °C (diethyl ether-hexanes); R_f 0.30 (ethyl acetate-hexanes 3:7 v/v); $[\alpha]_D$ -252° (c = 0.5, acetone, 20 °C); IR: ν N_3: 2100 cm^{-1}; ^1H NMR (DMSO-6d, 300 MHz) 5.41 (t, 1H exchangeable, $J_{OH,H-1}$ and $J_{OH,H-1'}$ 6.4, O<u>H</u>), 4.27 (dq, 1H, $J_{5,6}$ 2.6, H-5), 4.13 (dd, 1H, $J_{4,5}$ 5.7, H-4), 4.02 (dd, 1H, $J_{6,6'}$ 13.6, H-6'), 3.92 (dd, 1H, $J_{5,6'}$ 0.9, H-6), 3.67 (d, 2H, H-1, H-1'), 3.42 (s, 3H, OMe), 3.36 (d, 1H, $J_{3,4}$ 7.3, H-3), 1.45, 1.29 (2s, 6H, methylethylidene); ^{13}C NMR ($CDCl_3$) 64.8, 61.8 (C-1, C-6), 92.0 (C-2), 78.7, 73.2, 76.5 (C-3 to C-5), 60.2 (OMe), 109.3, 28.1, 26.2 (methylethylidene).

Anal.: Calcd. for $C_{10}H_{17}O_5N_3$: C, 46.33; H, 6.61; O, 30.86; N, 16.21; found: C, 46.54; H, 6.74; O, 30.80; N, 16.19.

1-O-Acetyl-3-O-methyl-4,5-O-methylethylidene-α- and -β-D-fructopyranosyl azides **4**α and **4**β. Acetic anhydride (8 mL) was added under stirring to a pyridine solution (16 mL) containing an anomeric mixture of **3** (1.38 g, 7.5 mmol, α/β ratio ~1/10). After 14 h, crushed ice was added and the organic material were taken up in diethyl ether. Washing the ethereal phase several times with brine, then drying and concentration afforded a residue which was applied to a column eluted with ethyl acetate-hexanes 2:8 v/v to give first **4**β (1.386 g, 86 %) then **4**α (133 mg, 8 %).

4α: colourless syrup; R_f 0.59 (ethyl acetate-hexanes 3:7 v/v); $[\alpha]_D$ +43° (c = 0.8, acetone, 20 °C); IR: ν N_3: 2105 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) 4.52 (d, 1H, $J_{1,1'}$ 11.8, H-1), 4.31 (d, 1H, H-1'), 4.02 (t, 1H, $J_{4,5}$ 6.8, H-4), 3.90 (dt, 1H, $J_{5,6}$ 5.2, H-5), 3.71 (m, 2H, $J_{5,6'}$ 5.2, $J_{6,6'}$ ~13, H-6, H-6'), 3.38 (d, 1H, $J_{3,4}$ 6.5, H-3), 3.24 (s, 3H, OMe), 1.70 (s, 3H, acetyl), 1.44, 1.17 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6) 64.1, 62.9 (C-1, C-6), 91.1 (C-2), 81.8, 71.7, 75.2 (C-3 to C-5), 59.9 (OMe), 109.8, 27.3, 25.1 (methylethylidene), 169.6, 20.1 (acetyl).

Anal.: Calcd. for $C_{12}H_{19}O_6N_3$: C, 47.84; H, 6.36; O, 31.86; N, 13.95; found: C, 47.71; H, 6.46; O, 31.92; N, 13.87.

4β: white solid, mp 77.5 °C (diethyl ether-hexanes); R_f 0.62 (ethyl acetate-hexanes 3:7 v/v); $[\alpha]_D$ -205° (c = 0.75, acetone, 20 °C); IR: ν N_3: 2105 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) 4.61 (d, 1H, $J_{1,1'}$ 11.5, H-1), 4.46 (d, 1H, H-1'), 4.13 (dd, 1H, $J_{4,5}$ 5.6, H-4), 3.86 (dd, 1H, $J_{6,6'}$ 14.3, H-6'), 3.69 (dd, 1H, $J_{5,6'}$ 2.5, H-6), 3.68 (m, 1H, $J_{5,6}$ 2.9, H-5), 3.352 (d, 1H, $J_{3,4}$ 7.1, H-3), 3.349 (s, 3H, OMe), 1.71 (s, 3H, acetyl), 1.41, 1.19 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6) 65.4, 62.1 (C-1, C-6), 91.4 (C-2), 80.0, 73.3, 76.6 (C-3 to C-5), 59.7 (OMe), 109.1, 28.0, 26.0 (methylethylidene), 169.5, 20.1 (acetyl).

Anal.: Calcd. for $C_{12}H_{19}O_6N_3$: C, 47.84; H, 6.36; O, 31.86; N, 13.95; found: C, 47.85; H, 6.36; O, 31.91; N, 14.01.

1,2:4,5-Di-O-methylethylidene-3-O-thiomethylthiocarbonyl-β-D-fructopyranose **5** . This xanthogenate derivative was prepared according to a literature procedure[18] in a 76 % yield. R_f 0.51 (ethyl acetate-hexanes 1:5 v/v, reddish spot). ^1H NMR ($CDCl_3$, 300 MHz) 6.06 (d, 1H, $J_{3,4}$ 7.95, H-3), 4.47 (dd, 1H, $J_{4,5}$ 5.3, H-4), 4.28 (m, 1H, $J_{5,6}$ 2.5, H-5), 4.18 (dd, 1H, $J_{5,6'}$ ~0, H-6), 4.11 (d, 1H, $J_{6,6'}$ 13.5, H-6'), 3.94 (s, 2H, H-1, H-1'), 2.60 (s, 3H, SMe), 1.580, 1.506, 1.408, 1.367 (4s, 12H, methylethylidene); ^{13}C NMR ($CDCl_3$) 71.3, 60.2 (C-1, C-6), 103.6 (C-2), 78.3, 73.9, 74.8 (C-3 to C-5), 112.2, 109.8, 27.7, 26.6, 26.3, 25.9 (isopropylidene), 217.1, 19.2 (*O*-thiocarbonylthiomethyl).

1,2:4,5-Di-O-methylethylidene-3-thio-3-S-thiomethylcarbonyl-β-D-fructopyranose **6**. During an unoptimized synthesis of **7**[18] (41 % from **5**) by the Barton-McCombie reaction, using, however, nitrogen instead of argon as the inert gas, compound **6** was formed as a byproduct (12 %) which was separated by column chromatography. R_f 0.44 (ethyl acetate-hexanes 1:5 v/v, black spot). ^1H NMR ($CDCl_3$, 300 MHz) 5.16 (d, 1H, $J_{3,4}$ 7.8, H-3), 4.31 (dd, 1H, $J_{4,5}$ 5.3, H-4), 4.23 (dd, 1H, $J_{5,6}$ 2.3, H-5), 4.14 (dd, 1H, $J_{5,6'}$ ~0, H-6), 4.07 (d, 1H, $J_{6,6'}$ 13.3, H-6'), 3.98 (d, 1H, $J_{1,1'}$ 9.3, H-1), 3.88 (d, 1H, H-1'), 2.36 (s, 3H, SMe), 1.57, 1.49, 1.41, 1.37 (4s, 12H, methylethylidene); ^{13}C NMR ($CDCl_3$) 71.5, 60.2 (C-1, C-6), 103.3 (C-2), 73.0, 73.7, 74.7 (C-3 to C-5), 112.3, 109.6, 27.8, 26.5, 26.2, 25.8 (methylethylidene), 171.8, 13.4 (*S*-carbonylthiomethyl).

*3-Deoxy-1,2:4,5-di-O-methylethylidene-β-D-*erythro-*hex-2-ulopyranose* **7**. Compound **7** was prepared from **5** as described[18] (Bu_3SnH, AIBN, argon atmosphere) in a 68 % yield. R_f 0.31 (ethyl acetate-hexanes 1:5 v/v, yellowish spot). ^1H NMR ($CDCl_3$, 300 MHz) 4.47 (dq, 1H, $J_{4,5}$ 6.65, H-4), 4.13 (dt, 1H, $J_{5,6}$ 1.5, H-5), 4.07 (d, 1H, $J_{1,1'}$ 8.85, H-1), 3.89 (m, 2H, $J_{5,6'}$ ~1.5, H-6, H-6'), 3.83 (d, 1H, H-1'), 2.08 (dd, 1H, $J_{3,4}$ 5.65, $J_{3,3'}$ 14.5, H-3), 2.00 (dd, 1H, $J_{3',4}$ 4.55, H-3'), 1.49, 1.48, 1.38, 1.34 (4s, 12H, methylethylidene). Use of Bu_3SnD afforded a ~3/1 mixture of ^2H isotopomers at C-3. Depletion of the δ 1.99 ppm resonance (m, $J_{3e,4}$ 4.3, H-3e, 23 %) as compared to the major signal (δ 2.05, m, $J_{3a,4}$ 5.7, H-3a, 77 %) observed by ^1H NMR spectroscopy showed the higher proportion of the isomer having a equatorial C—D bond. ^{13}C NMR ($CDCl_3$) 76.2, 62.2 (C-1, C-6), 103.2 (C-2), 34.2 (C-3), 70.1, 71.9 (C-4, C-5), 110.1, 108.7, 27.1, 26.6, 26.5, 25.3 (methylethylidene).

*3-Deoxy-4,5-O-methylethylidene-α- and -β-D-*erythro-*hex-2-ulopyranosyl azides* **9α** and **9β**. Trimethylsilyl azide (1.6 mL, 12 mmol) was added under stirring to an acetonitrile solution (40 mL) cooled to 0 °C and containing **7** (975 mg, 4 mmol). Half an hour after trimethylsilyl triflate addition (0.22 mL, 1.2 mmol, in 5 mL acetonitrile), temperature was allowed to raise to normal. Completion of the reaction was reached within 1 h, as indicated by the presence of three more mobile spots on TLC plates (ethyl acetate-hexanes 3:7 v/v). Successive additions of triethylamine (0.35 mL, 2.4 mmol) and potassium fluoride (0.7 g, 12 mmol, in 3 mL water) resulted, on stirring overnight, in desilylation which was not entirely selective as judged from the presence on TLC plates of several minor spots corresponding to unidentified polar products. After partial evaporation of acetonitrile under vacuum, the residue was extracted with diethyl ether (3 x 50 mL). The combined phases were washed twice with brine, then dried (Na_2SO_4) and concentrated. Resolution of the mixture (686 mg, 75 %) was achieved by column chromatography (ethyl acetate-hexanes 3:7 v/v) to afford first anomer **9β** (229 mg, 25 %), then 86 mg of **9α** (~6 %) in admixture, presumably, with a 2,3-unsaturated impurity. This was suggested by the presence of deshielded signals in the ^1H NMR spectrum [C_6D_6, 5.0 (dt, 1H, $J_{3,4}$ 4, $J_{3,1}$ ~$J_{3,1'}$ ~1, H-3), 4.24 (br. t, 1H, $J_{4,5}$ ~5, H-4)], showing ^4J couplings with H-1 and H-1' through a C=C double bond.

9β: colourless oil; $[\alpha]_D$ -175° (c = 1.1, acetone, 20 °C); IR: ν N_3: 2100 cm^{-1}; R_f 0.30 (ethyl acetate-hexanes 3:7 v/v); ^1H NMR (C_6D_6, 300 MHz) 3.89 (dt, 1H, $J_{4,5}$ 6.8, H-4), 3.67 (dd, 1H, $J_{5,6'}$ 2.55, H-6), 3.61 (m, 2H, H-1, H-1'), 3.49 (dq, 1H, $J_{5,6}$ 1.3, H-5), 3.36 (dd, 1H, $J_{6,6'}$ 13.1, H-6'), 2.05 (broad t, 1H, O<u>H</u>), 1.867 (dd, 1H, $J_{3,4}$ 5.43, $J_{3,3'}$ 14.95, H-3), 1.40 (s, 3H, methylethylidene), 1.312 (dd, 1H, $J_{3',4}$ 4.75, H-3'), 1.129 (s, 3H, methylethylidene); ^{13}C NMR (C_6D_6) 68.6, 63.3 (C-1, C-6), 91.8 (C-2), 31.0 (C-3), 69.5, 71.8 (C-4, C-5), 108.8, 27.0, 25.1 (methylethylidene).

Anal.: Calcd. for $C_9H_{15}O_4N_3$: C, 47.14; H, 6.62; O, 27.92; N, 18.33; found: C, 46.53; H, 6.76; O, 28.91; N, 17.98.

*1-O-Acetyl-3-deoxy-4,5-O-methylethylidene-α- and -β-D-*erythro*-hex-2-ulopyranosyl azides* **10α** and **10β**. Azides **9α** and **9β** were prepared from **7** (1.7 g, 7 mmol) as indicated above. However, after addition of triethylamine (0.6 mL, 4.2 mmol), pyridine (28 mL), acetic anhydride (17 mL) and tetra-*n*-butyl ammonium fluoride (11g, 35 mmol) were successively added. The reaction mixture was stirred for 3 h at room temperature whereupon crushed ice was added. After ~1h, the obtained liquid phase was concentrated under diminished pressure and the residue was extracted with diethyl ether (3 x 50 mL). The combined phases were washed (brine), dried, concentrated and the residual oil was applied to a column (diethyl ether-petroleum ether 1:4 v/v) to afford **10β** (0.915g, 49 %), **10α** (75 mg, 4 %) and **11** (175 mg, 8 %).

10α: colourless oil; R_f 0.20 (diethyl ether-petroleum ether 1:4 v/v); $[\alpha]_D$ +90° (c = 0.2, acetone, 20 °C); IR: ν N_3: 2110 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) 4.09 (d, 1H, $J_{1,1'}$ 11.5, H-1), 3.92 (d, 1H, H-1'), 3.84 (q, 1H, $J_{3,4}$ 5, $J_{3',4}$ 5, $J_{4,5}$ 10.6, H-4), 3.75 (dd, 1H, $J_{6,6'}$ ~14, $J_{5,6}$ ~1.5, H-6), 3.70 (dd, 1H, $J_{5,6'}$ ~1.2, H-6'), 3.49 (m, 1H, H-5), 1.90 (dd, 1H, $J_{3,3'}$ 15.2, H-3), 1.63 (s, 3H, acetyl), 1.47 (dd, 1H, H-3'), 1.45, 1.16 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6) 67.9, 62.9 (C-1, C-6), 88.6 (C-2), 31.6 (C-3), 69.9, 70.2 (C-4, C-5), 109.4, 27.7, 25.3 (methylethylidene), 169.5, 20.1 (acetyl).

Anal.: Calcd. for $C_{11}H_{17}O_5N_3$: C, 48.70; H, 6.32; O, 29.49; N, 15.49; found: C, 48.67; H, 6.55; O, 30.39; N, 15.45.

10β: colourless oil; R_f 0.25 (diethyl ether-petroleum ether 1:4 v/v); $[\alpha]_D$ -124° (c = 0.9, acetone, 20 °C); IR: ν N_3: 2110 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) 4.68 (d, 1H, $J_{1,1'}$ 11.5, H-1), 4.16 (d, 1H, H-1'), 3.88 (dq, 1H, $J_{4,5}$ 7.2, H-4), 3.65 (dd, 1H, $J_{5,6'}$ 2.5, H-6), 3.50 (dq, 1H, $J_{5,6}$ 1.2, H-5), 3.31 (dd, 1H, $J_{6,6'}$ 13, H-6'), 1.83 (dd, 1H, $J_{3,4}$ 5.05, $J_{3,3'}$ 15.1, H-3), 1.66 (s, 3H, acetyl), 1.44 (s, 3H, methylethylidene), 1.31 (dd, 1H, $J_{3',4}$ 4.35, H-3'), 1.13 (s, 3H, methylethylidene); ^{13}C NMR (C_6D_6) 68.4, 63.3 (C-1, C-6), 90.3 (C-2), 31.2 (C-3), 69.3, 71.8 (C-4, C-5), 108.9, 26.9, 25.0 (methylethylidene), 169.4, 20.1 (acetyl).

Anal.: Calcd. for $C_{11}H_{17}O_5N_3$: C, 48.70; H, 6.32; O, 29.49; N, 15.49; found: C, 49.06; H, 6.29; O, 30.32; N, 14.44.

11: R_f 0.17 (diethyl ether-petroleum ether 1:4 v/v); $[\alpha]_D$ -165° (c = 0.8, acetone, 20 °C); IR: ν N_3: 2110 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) 5.21 (dq, 1H, $J_{4,5}$ 3.0, H-4), 5.15 (m, 1H, $J_{5,6}$ 1.4, H-5), 4.26 (d, 1H, $J_{1,1'}$ 11.6, H-1), 4.04 (d, 1H, H-1'), 3.52 (dd, 1H, $J_{5,6'}$ 2.1, $J_{6,6'}$ 13.25, H-6'), 3.32 (dd, 1H, H-6), 1.75 (t, 1H, $J_{3a,4}$ 12.0, H-3a), 1.69, 1.65, 1.63 (3s, 9H, acetyl), 1.59 (ddd, 1H, $J_{3e,4}$ 5.0, $J_{3a,3e}$ 12.6, $J_{3e,5}$ 0.8, H-3e); ^{13}C NMR (C_6D_6) 67.7, 64.1 (C-1, C-6), 91.6 (C-2), 31.1 (C-3), 66.1, 66.9 (C-4, C-5), 169.3, 169.3, 169.6, 20.0, 20.4, 20.5 (acetyl).

Anal.: Calcd. for $C_{12}H_{17}O_7N_3$: C, 45.72; H, 5.43; O, 35.52; N, 13.33; found: C, 45.30; H, 5.41; O, 34.78; N, 13.56.

1-O-Methanesulfonyl-3-O-methyl-4,5-O-methylethylidene-β-D-fructopyranosyl azide **12**. To an ice-cooled dichloromethane solution (1 mL) containing **3β** (282 mg, 1.09 mmol), pyridine (0.35 mL) then methanesulfonyl chloride (0.15 mL, 2 mmol) were added. After stirring overnight, crushed ice was added to the reaction mixture which was extracted after 1 h with diethyl ether (4 x 25 mL). The combined organic phases were dried (Na_2SO_4), evaporated and the residue was applied to a column eluted with ethyl acetate-hexanes 3:7 v/v to afford **12** (317 mg, 87 % yield). Colourless prisms, mp 90-91°C (diethyl ether-petroleum ether); R_f 0.27 (diethyl ether-petroleum ether 1:1 v/v); $[\alpha]_D$ -139° (c = 0.6, acetone, 21°C); IR: ν N_3: 2120 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 4.52 (d, 1H, $J_{1,1'}$ 10.9, H-1), 4.45 (d, 1H, H-1'), 4.31 (t, 1H, $J_{4,5}$ 5.6, H-4), 4.29 (dq, 1H, $J_{5,6}$ 2.5, H-5), 4.15 (dd, 1H, $J_{6,6'}$ 13.6, H-6'), 4.09 (dd, 1H, $J_{5,6'}$ 1.3, H-6), 3.58 (s, 3H, OMe), 3.43 (d, 1H, $J_{3,4}$ 6.5, H-3), 3.12 (s, 3H, OMs), 1.55, 1.38 (2s, 6H, methylethylidene); ^{13}C NMR ($CDCl_3$) 69.4, 62.2 (C-1, C-6), 90.5 (C-2), 75.9, 72.7, 77.9 (C-3 to C-5), 109.5, 27.8, 25.9 (methylethylidene), 38.0 (mesyl).

Anal.: Calcd. for $C_{11}H_{19}O_7N_3S$: C, 39.16; H, 5.68; O, 33.20; N, 12.46; S, 9.50; found: C, 39.19; H, 5.74; O, 33.24; N, 12.62; S, 9.29.

1,4,5-Tri-O-acetyl-3-O-methyl-β-D-fructopyranosyl azide **13**. Compound **3β** (27 mg, 0.104 mmol) treated with acetic anhydride and 70 % $HClO_4$ according to a described procedure[21] yielded **13** (20.5 mg, 57 % yield) which was examined by NMR prior to photolysis. ^1H NMR ($CDCl_3$, 300 MHz) 5.34 (m, 1H, $J_{5,6}$ 1.8, H-5), 5.22 (dd, 1H, $J_{4,5}$ 3.3, H-4), 4.53 (d, 1H, $J_{1,1'}$ 11.6, H-1), 4.44 (d, 1H, H-1'), 4.025 (dd, 1H, $J_{6,6'}$ 13.3, H-6'), 3.89 (dd, 1H, $J_{5,6'}$ 1.2, H-6), 3.63 (d, 1H, $J_{3,4}$ 10.1, H-3), 3.52 (s, 3H, OMe), 2.174, 2.158, 2.068 (3s, 9H, acetyl).

Photolyses. Solutions containing the substrates were poured in quartz tubes (1 cm diameter) placed at ~1 cm of a 450 W medium-pressure mercury lamp (Hanovia) delivering unfiltered light. MeOH, CH_3CN and C_6H_6, either normal or deuterated were used as the solvent. In this case, after reaction

completion was reached as shown by TLC monitoring, the solution was transfered to a NMR tube for examination. Based on comparison of the area of well-separated, characteristic signals (H-1, H-1', H-3 and methyl groups) as well as those corresponding to unidentified byproducts, the NMR yield of ring-expanded product / iminolactone, if observed, were as follows, depending on starting material, solvent and irradiation time: **3β** (C_6D_6, 1.5 h): ~10 / 0; **4β** (C_6H_6, 1.5 h): 74 / 7; **4β** (C_6D_6, 1.5 h): 72 / 7.5; **4β** (CD_3CN, 1.5 h): 65 / 0; **4β** (CD_3OD[22], 2 h): 56 / 13; **4α** (C_6D_6): 59 / 22; **9α** (C_6D_6, 2.25 h): not determined; **9β** (C_6D_6, 2.25 h): not determined; **10α** (C_6D_6, 3.25 h): ~50 / 0; **10β** (C_6D_6, 2.25 h): ~50 / 10, in admixture with ~25 % unchanged **10β**, (C_6D_6, 4.5 h): ~50 / 0; **12** (C_6D_6, 3.5 h): 35 / 6; **13** (C_6D_6): 35 / 0. NMR data extracted from the spectra of the obtained crude reaction mixtures are listed below:

*photolysis of **3β** in C_6D_6*: Besides multiplets from 1.0 to 1.7 and 2.8 to 5.0 ppm, a dt appeared at 4.90 ($J_{3,1}$ ~$J_{3,1'}$ 1.4, $J_{3,4}$ 7.7, H-3).

*photolysis of either **4α** or **4β***: major product: **14**A: ^{1}H NMR (C_6D_6, 300 MHz) 5.01 (dt, 1H, $J_{3,4}$ 8.0, $J_{3,1}$ 1.45, $J_{3,1'}$ 1.25, H-3), 4.47 (dd, 1H, $J_{1,1'}$ 14.4, H-1), 4.38 (dd, 1H, H-1'), 4.37 (dd, 1H, $J_{4,5}$ 7.0, H-4), 4.02 (dq, 1H, $J_{5,6}$ 10.3, H-5), 3.94 (t, 1H, $J_{5,6'}$ 3.1, H-6), 3.69 (dd, 1H, $J_{6,6'}$ 11, H-6'), 3.39 (s, 3H, OMe), 1.78 (s, 3H, acetyl), 1.36, 1.08 (2s, 6H, methylethylidene). A 3.5 % enhancement of the H-3 signal was observed on irradiation of the OMe proton in nOe difference spectra. ^{13}C NMR (C_6D_6, 75 MHz) 66.4, 62.3 (C-1, C-6), 151.4 (C-2), 86.5, 72.6, 78.8 (C-3 to C-5), 54.9 (OMe), 170.3, 20.7 (acetyl), 110.0, 27.1, 24.4 (methylethylidene); minor product: **15**A: ^{1}H NMR (C_6D_6, 300 MHz) 5.78 (d, 1H, $J_{1,1'}$ 12.5, H-1), 5.63 (d, 1H, H-1'), 4.15 (dd, 1H, $J_{4,5}$ 7.5, H-4), 4.06 (dd, 1H, $J_{6,6'}$ 12, H-6'), 3.86 (dd, 1H, $J_{5,6'}$ 1.6, H-6), 3.74 (dt, 1H, $J_{5,6}$ 1.5, H-5), 3.68 (d, 1H, $J_{3,4}$ 2.2, H-3), 3.11 (s, 3H, OMe), 1.74 (s, 3H, acetyl), 1.41, 1.05 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6, 75 MHz) 66.2, 62.0 (C-1, C-6), 153.1 (C-2), 73.8, 71.8, 77.5 (C-3 to C-5), 57.4 (OMe), 170.7, 21.2 (acetyl), 110.1, 26.1, 24.1 (methylethylidene).

*photolysis of either **9α** or **9β** in C_6D_6*: In each spectrum, besides multiplets, the only clear signals were as follows: 2.98 (dd, J_{gem} 12.8, J 2.0) and 2.44 (dd, J_{gem} 15.8, J 2.5).

*photolysis of either **10α** or **10β***: **16**: ^{1}H NMR (C_6D_6, 300 MHz) 4.55 (dt, 1H, $J_{1,1'}$ 14.3, $J_{1,3e} \approx J_{1,3a} \approx 1$, H-1), 4.47 (dt, 1H, $J_{1',3e} \approx J_{1',3a} \approx 0.9$, H-1'), 4.02 (dt, 1H, $J_{4,3e}$ 2.3, $J_{4,3a}$ 7.2, $J_{4,5}$ ~7.2, H-4), 3.79 (dd, 1H, $J_{3a,4}$ 7.1, $J_{3a,3e}$ 15.8, H-3a), ~3.77 (m, 2H, H-5, H-6), 3.68 (dd, 1H, $J_{5,6'}$ 1.7, $J_{6,6'}$ 11.6, H-6'), 3.49 (dm, 1H, $J_{3e,4}$ 2.5, H-3e), 1.76 (s, 3H, acetyl), 1.44, 1.15 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6, 75 MHz) 68.0, 62.5 (C-1, C-6), 153.8 (C-2), 77.1, 75.2 (C-4, C-5), 46.7 (C-3), 169.7, 21.8 (acetyl), 109.2, 27.2, 25.0 (methylethylidene); **17**: ^{1}H NMR (C_6D_6, 300 MHz) 5.79 (dd, 1H, $J_{1,1'}$ 11.8, $J_{1,3e}$ 2.5, H-1), 5.62 (dd, 1H, $J_{1',3e}$ 2.1, H-1').

*photolysis of **12***: main compound **14**B: ^{1}H NMR (C_6D_6, 300 MHz) 4.88 (dt, 1H, $J_{3,4}$ 7.85, $J_{1,3}$ 1.1, $J_{1',3}$ 1.3, H-3), 4.34 (dd, 1H, $J_{1,1'}$ 14.4, H-1), 4.267 (dd, 1H, H-1'), 4.273 (dd, 1H, $J_{4,5}$ ~7, H-4), 3.93 (dq, 1H, $J_{5,6}$ ~10, $J_{5,6'}$ 3.2, H-5), 3.83 (t, 1H, $J_{6,6'}$ 11.5, H-6), 3.63 (dd, 1H, H-6'), 3.29 (s, 3H, OMe), 2.54 (s, 3H, mesyl), 1.35, 1.09 (2s, 6H, methylethylidene); ^{13}C NMR (C_6D_6, 75 MHz) 67.0, 66.8 (C-1, C-6), 150.7 (C-2), 87.2, 73.2, 79.2 (C-3 to C-5), 55.2 (OMe), 38.5 (mesyl), 109.7, 27.2, 24.5 (methylethylidene); minor compound **15**B: ^{1}H NMR (C_6D_6, 300 MHz) 5.09 (d, 1H, J_{gem} 12.8, H-1), 5.01 (d, 1H, J_{gem} 12.8, H-1'), 3.05 (s, 3H, OMe), 2.47 (s, 3H, mesyl), 1.49, 1.02 (2s, 3H, methylethylidene); ^{13}C NMR (C_6D_6, 75 MHz) 157.9 (C-2).

*photolysis of **13***: main compound: ^{1}H NMR (C_6D_6, 300 MHz) 5.26 (m, 1H, $J_{5,6}$ 4.5, $J_{5,6'}$ 1.4, H-5), 5.21 (dd, 1H, $J_{4,5}$ 3.1, H-4), 5.05 (dt, 1H, $J_{3,4}$ 8.8, $J_{3,1}$ 1.9, $J_{3,1'}$ 1.9, H-3), 4.43 (dd, 1H, $J_{1,1'}$ 15.2, H-1), 4.34 (dd, 1H, H-1'), 3.65 (dd, 1H, $J_{6,6'}$ 13.3, H-6), 3.36 (s, 3H, OMe), 3.13 (dd, 1H, H-6'), 1.76, 1.63, 1.58 (3s, 9H, acetyl).

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