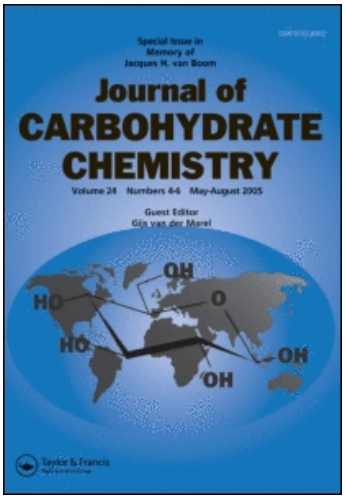

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RADICAL-MEDIATED HALOGENATIONS OF ANOMERICALLY N-SUBSTITUTED GLUCOPYRANOSYL DERIVATIVES.

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ABSTRACT

Reactions of acetylated *N*-aryl-D-glucosylamines with *N*-bromosuccinimide-benzoyl peroxide or with sulfuryl chloride-azoisobutyronitrile gave aromatic halo derivatives. The corresponding *N*-acetylated compounds were mostly inert towards halogenation. Bromination of acetylated cellobiosylpiperidine resulted in the formation of acetobromocellobiose, while the acetylated 2,6,8-trichloro-9-(β-D-glucopyranosyl)-purine was transformed into its 5'-bromo derivative. In contrast, peracetylated glucopyranosyl isothiocyanate or azides, when treated by *N*-bromosuccinimide under free-radical conditions, essentially undergo an initial homolysis of the anomeric C-H bond which is faster for β-anomers. This initiates a new , simple and efficient free-radical transformation of such sugar azides into an unprecedented bromimino lactone (92% isolated yield).

INTRODUCTION

Radical-mediated brominations at ring positions of carbohydrates[1] have been known for about 15 years. Brominations of uronic acid derivatives, peracylated aldoses, anhydro sugar derivatives, glyculoses and glycosuloses, *C*-glycosyl heterocycles and

glycosyl cyanides, glycosyl halides, glycopyranoside esters, 1-thio-glycoside esters, glucopyranosyl phenyl sulfoxides and sulfones and several disaccharides were performed either with *N*-bromosuccinimide (NBS) or bromine (Br_2) in refluxing carbon tetrachloride in the presence of chemical initiators such as benzoyl peroxide (Bz_2O_2) or azoisobutyronitrile (AIBN) and/or by photoinitiation. Some chlorinations were carried out with sulfuryl chloride (SO_2Cl_2)-AIBN. Most reactions took place at C-1 or C-5 of the pyranoid ring, and the halides contained an axial carbon-halogen bond.

Stabilizing effects of substituents of different character (c = acceptor : CN, CO_2Me, COR, NO_2, etc.; d = donor : OR, NR_2, SR, etc.) at carbon radical centres and especially joint actions of pairs of substituents (cc, dd, cd) attracted considerable attention recently.[2,3] Application of these considerations to explain the outcomes of the carbohydrate brominations was also attempted.[1,4] It can be briefly concluded that cd substituted centres react readily to give high yields of the bromo derivatives. The effect of oxygen-oxygen dd pairs at the anomeric centre depends upon the substituent on the glycosidic oxygen atom. Methyl glycoside derivatives react at C-1, but C-5 substitution is favoured for glycosyl esters and aromatic glycosides.

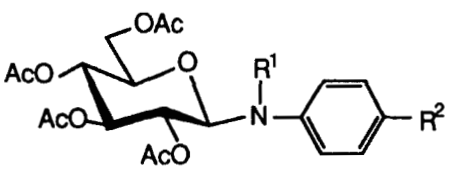
The very good stabilization of carbon radicals by amino substituents is well-known.[5,6] Among the investigated carbohydrate derivatives with a nitrogen substituent at the anomeric centre, adenosine pentabenzoate is the only compound described to give a 4'-bromo product[7] by photobromination. Therefore we have undertaken to brominate some glucosylamines and other *N*-substituted glucopyranosyl derivatives.

RESULTS AND DISCUSSION

The readily available[8,9] acetylated *N*-aryl-D-glucosylamines (**1-4**) as well as their *N*-acetylated derivatives (**5-8**) (SCHEME 1) were brominated with NBS in refluxing carbon tetrachloride in the presence of catalytic benzoyl peroxide (method A).

The anilino compound **1** gave in a relatively short time of reaction two products from which only one has been isolated by crystallization (TABLE 1). In its mass spectrum m/e = 580, 582, 584 $(M+1)^+$ peaks could be observed with an intensity ratio ~ 1 : 2 : 1 indicating the presence of two bromine atoms. Since the proton spectrum contained resonances for each sugar proton + NH and in the aromatic region two doublets and one double doublet characteristic for a 1,2,4-trisubstitution pattern appeared, aromatic dibromination was concluded. Having in mind that bromination of different aniline derivatives with NBS[10,11] preferably leads to substitution in positions 2 and/or 4 of the aromatic ring, we prefer to suggest structure **9** for this compound. This is

SCHEME 1



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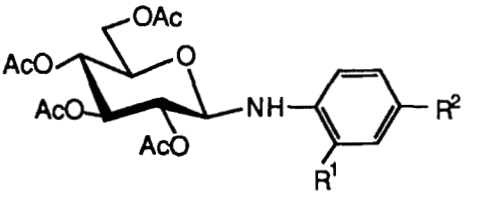
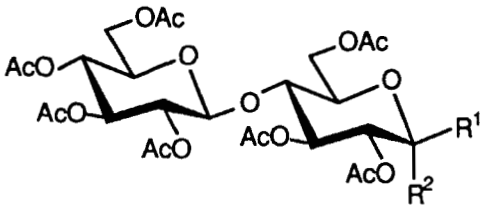


9 - 13

	R^1	R^2
1	H	H
2	H	CH_3
3	H	OCH_3
4	H	NO_2

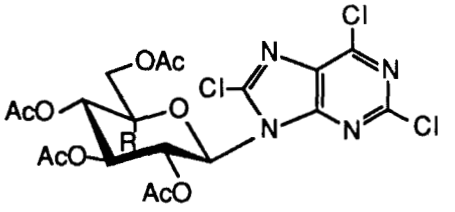
	R^1	R^2
5	Ac	H
6	Ac	CH_3
7	Ac	OCH_3
8	Ac	NO_2
14	Ac	$CH_nBr_{(3-n)}$ n = 0,1,2

	R^1	R^2
9	Br	Br
10	Cl	Cl
11	Br	CH_3
12	Br	OCH_3
13	Cl	NO_2



15 $R^1 = -N\bigcirc$, $R^2 = H$

16 $R^1 = H$, $R^2 = Br$



17 R = H

18 R = Br

also supported by the comparison with the proton chemical shifts for 2,4-dibromoaniline showing about 0.1-0.15 ppm difference for each proton. The proton spectrum of the mother liquor contained resonances in addition to those of **9** at 6.99 (d, 9 Hz, 1H), 7.32 (dd, 1H) and 7.60 (d, 2Hz, 1H) indicating the presence of an isomeric dibromo but not isolated product. Chlorination of **1** with SO_2Cl_2/AIBN (method F) resulted in the analogous dichloro product **10**, together with an unidentified isomer.

Bromination of **2** gave two products each of which had m/e = 515, 517 $(M)^+$ peaks in their mass spectra indicating a monobromination. The large difference in the chemical

TABLE 1: Reactions of *N*-glycosylamine derivatives under radical-mediated halogenation conditions.

Starting Compound	Isolated compound	Method[a]	Reaction time(h)	Yield (%)	Mp (°C)	$[\alpha]^{20}$ b	Formula	Analysis	Calcd	Found
1	**9**	A	1	42	189-191	-52	$C_{20}H_{23}Br_2NO_9$	Br : N :	27.49 2.40	27.09 2.30
1	**10**	F	0.5	28	163-165	-5	$C_{20}H_{23}Cl_2NO_9$	Cl: N :	14.43 2.85	14.51 2.71
2	**11β+11α** **11β**	A	2	83 34	138-140	-46	$C_{21}H_{26}BrNO_9$	Br : N :	15.50 2.71	15.40 2.51
	11α			9	syrup	+121	$C_{21}H_{26}BrNO_9$	Br: N :	15.50 2.71	16.20 2.62
3	**12**	A	1	78	167-168	-50	$C_{21}H_{26}BrNO_{10}$	Br : N :	15.03 2.63	14.83 2.63
4	**4**	A	16	68	153-154 (155 ref.9)					
4	**13**	F	0.5	30	155-156	-94	$C_{20}H_{23}ClN_2O_{11}$	Cl : N :	6.97 5.57	7.04 5.42
5	**5**	A	9	57	106-107 (100 ref.9)					

6	14	A	2	62	162-164			see text		
7	7	A	9	90	186-187 (185-186)[c]					
8	8	A	10	62	160-161 (161 ref.9)					
15	16	A	1	70	181-182 (183 ref.16)	+94 (+95.8)				
17	18	A	3	50	syrup	-64	$C_{19}H_{18}Cl_3BrN_4O_9$	Br: Cl : N :	12.63 16.80 8.85	12.52 16.68 8.61
19	20	E	6	46						
	21	E	6	25						
19	20	D	10	80						
19	20	B	8	25						
	22	B	8	60	see ref. 40					
19	23	F	12	60	syrup	-97	$C_{15}H_{18}O_9ClNS$	Cl : N :	8.36 3.30	8.91 3.45
24	25	F	5	55	syrup	-88	$C_{14}H_{18}O_9ClN_3$	Cl : N :	8.69 10.31	10.47 9.99
24	27	B	0.1	92	syrup		See ref. 20			

a. See Experimental; b. For chloroform solutions; c. Mixed mp with the starting material.

TABLE 2: ^{1}H NMR data of the isolated new compounds (for $CDCl_3$ solutions).

Compound	NH ($J_{NH,H1}$)	H-1 ($J_{H1,H2}$)	H-2 ($J_{H2,H3}$)	H-3 ($J_{H3,H4}$)	H-4 ($J_{H4,H5}$)	H-5 ($J_{H5,H6'}$)	H-6 ($J_{H5,H6}$)	H-6' ($J_{H6,H6'}$)	Arom.	OAc
9	5.41 8.1	4.68 8.7	5.16[a] 9.2	5.39[a] 9.2	5.11[a] 9.7	3.84 2.2	4.31 5.4	4.12 11.9	6.61 (d, 8.6Hz, 1H) 7.24 (dd, 1H) 7.53 (d, 2.1 Hz, 1H)	2.05 2.08 (12H)
10	5.42 8	4.71 9	5.15[a] 9.5	5.40[a] 9.5	5.11[a] 10	3.86 2.5	4.33 5.5	4.13 12.5	6.68 (d, 8.5Hz, 1H) 7.13 (dd, 1H) 7.30 (d, 2.5Hz, 1H)	2.06 (6H) 2.08 2.09
11β	5.22 8.5	4.69 8.5	5.16[a] 9	5.38[a] 9.5	5.11[a] 9.5	3.85 2.5	4.31 5	4.12 12	6.64 (d, 8Hz, 1H) 6.98 (dd, 1H) 7.26 (d, 2Hz, 1H)	2.05 2.07 2.10 (12 H) CH_3: 2.25
11α	4.99 2.5	5.31 5	5.18[a] 10	5.51[a] 10	5.12[a] 10	4.17 2	4.32 4.5	4.04 12	7.02 (s, 2H) 7.31 (s, 1H)	2.07 2.10 2.11 2.13 CH_3: 2.27

12	5.02 8.5	4.65 8.5	5.16[a] 8.5	5.38[a] 9.5	5.11[a] 9.5	3.84 2.5	4.31 5.5	4.12 12.5	6.71 (d, 9H, 1H) 6.80 (dd, 1H) 7.05 (d, 3Hz, 1H)	2.05 2.06 2.08 2.09 OCH3: 3.75
13	6.17 8	4.80 9	5.17[a] 9	5.43[a] 10	5.11[a] 10	3.90 2.5	4.32 5.5	4.13 12.5	6.77 (d, 9Hz, 1H) 8.09 (dd, 1H) 8.24 (d, 2.5Hz, 1H)	2.10 2.22 (12H)
18		6.42 2H, br s	9.5	5.75 10	5.52		4.56	4.45 12		1.89 2.07 2.16 (6H)
23		5.58 9.1	5.22 9.2	5.43 9.9	5.41		4.45	4.22 12.2		2.0 2.2
25		5.21 9.1	5.03 9.3	5.51 9.7	5.39		4.45	4.26 12.2		1.99 2.07 2.09 2.12

a. Tentative assignments.

TABLE 3: ^{13}C NMR data of the isolated new compounds (for $CDCl_3$ solutions).

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Others
18	74.75[a]	70.84[a]	67.84[a]	67.84[a]	97.35	64.91	153.61 153.21 151.00 143.25 Purin 169.42 168.74 C = 0 20.32 19.96 CH_3
22	157.2	139.6	126.2	64.2[a]	77.9[a]	62.0	170.4 , 169.7 , 168.2 : C = O 20.7 , 20.6, 20.3 : CH3
23	80.9	69.1[a]	69.8[a]	71.3[a]	99.0	64.8	169.8, 169.7, 169.1 : C =O 20.6, 20.5 : CH_3 145.4 : NCS
25	86.9	68.3[a]	69.9[a]	69.9[a]	99.6	64.9	169.7, 169.2, 169.1, 167.6 : C = O 20.6 , 20.5 , 20.4 : CH_3

a. Tentative assignments.

shifts for H-1 of these compounds as well as the different values of the 1,2-couplings together with a downfield shift of H-3 and H-5 suggest the formation of the epimeric monobrominated compounds **11**β and **11**α. It was not investigated whether this anomerization was due to any radical attack at C-1. Nevertheless, the known anomerization of per-*O*-acetylated *N*-aryl-glycosylamines[12] catalyzed by acids allows the assumption that the hydrogen bromide present at least in traces in the bromination mixtures can be responsible for this process. A somewhat similar epimerization was observed during radical-mediated bromination of an acetylated disaccharide.[13]

Bromination of **3** gave the aromatic bromo derivative **12** and the deactivated **4** was inert towards bromination, while its chlorination gave the aromatic chloro derivative **13**.

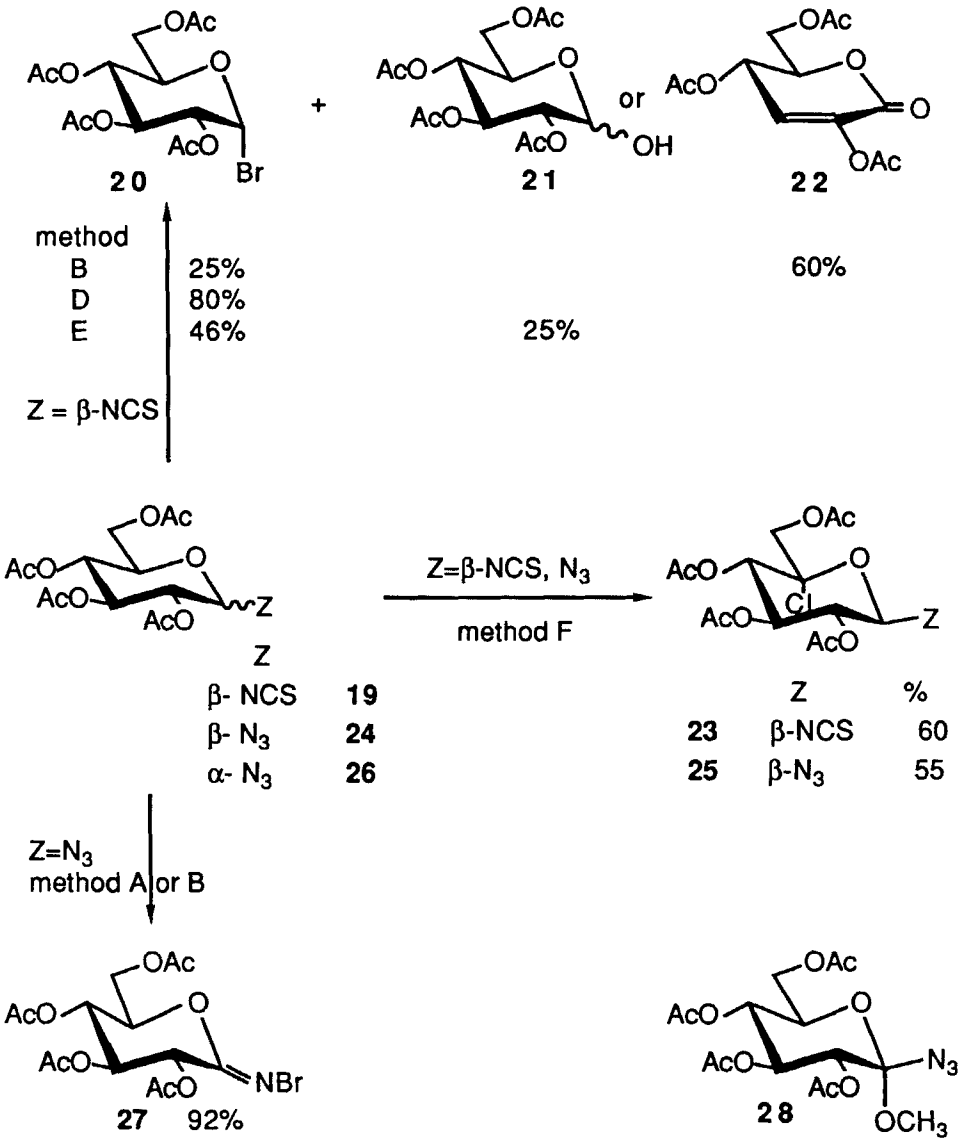
N-Acetylation as in compounds **5-8** leads to further deactivation of the aromatic rings so that no bromination occurred for rather long times and compounds **5**, **7** and **8** could be recovered by crystallization in reasonable yields (TABLE 1). From the bromination mixture of **6**, a crystalline substance was isolated. However, its proton spectrum, similar to that of **6**, exhibited resonances for each sugar and aromatic protons, but the intensity of the CH_3 signal (2.38) decreased and sharp singlets at 4.50 (CH_2Br) and 6.68 ($CHBr_2$) appeared indicating the presence of the corresponding compounds in a ratio 1 : 7 : 2. Elemental analysis of this substance (calcd for $C_{23}H_{27}Br_2NO_{10}$: Br : 25.08, found 25.44) suggests that even tribrominated products can be found in the mixture.

Bromination of hepta-*O*-acetyl-D-cellobiosylpiperidine[14] (**15**) gave clearly one product which according to its physical constants and spectral data proved to be the corresponding acetobromo disaccharide **16**.[16] Bromination of the purine glucopyranoside derivative **17**[15] took place at C-5 to give **18** as could be expected from a similar reaction of a benzoylated adenosine derivative,[7] and an unselective transformation was observed in the case of 2', 3', 5'-tri-*O*-benzoyl-uridine.

In summary, radical halogenation of *N*-aryl-glucopyranosylamines mainly occurs at the aromatic position of the aglycone without any reaction at the anomeric carbon of the carbohydrate moiety. α-Bromination was only observed in an example of one cellobiosyl derivative by an undetermined mechanism of substitution.

Photobromination of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate **19**[17] (SCHEME 2) has been studied in the presence of either bromine or *N*-bromosuccinimide. In the first case, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **20** (46 %) and 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose **21** (25 %) were isolated after a 6 h irradiation with a medium pressure mercury lamp (method E). A comparable transformation occurred by irradiating the reaction vessel with a sun lamp (method D) yielding essentially the α-bromide **20** (80 %). Compound **20** was also produced (25 %)

SCHEME 2



after prolonged treatment (8 h) of **19** in the presence of NBS (method B), along with the unsaturated lactone **22** (60 %). However, boiling a carbon tetrachloride solution of **19** in the presence of sulfuryl chloride (method F) and AIBN led to the C-5 chlorinated[18] compound **23** (60 %).

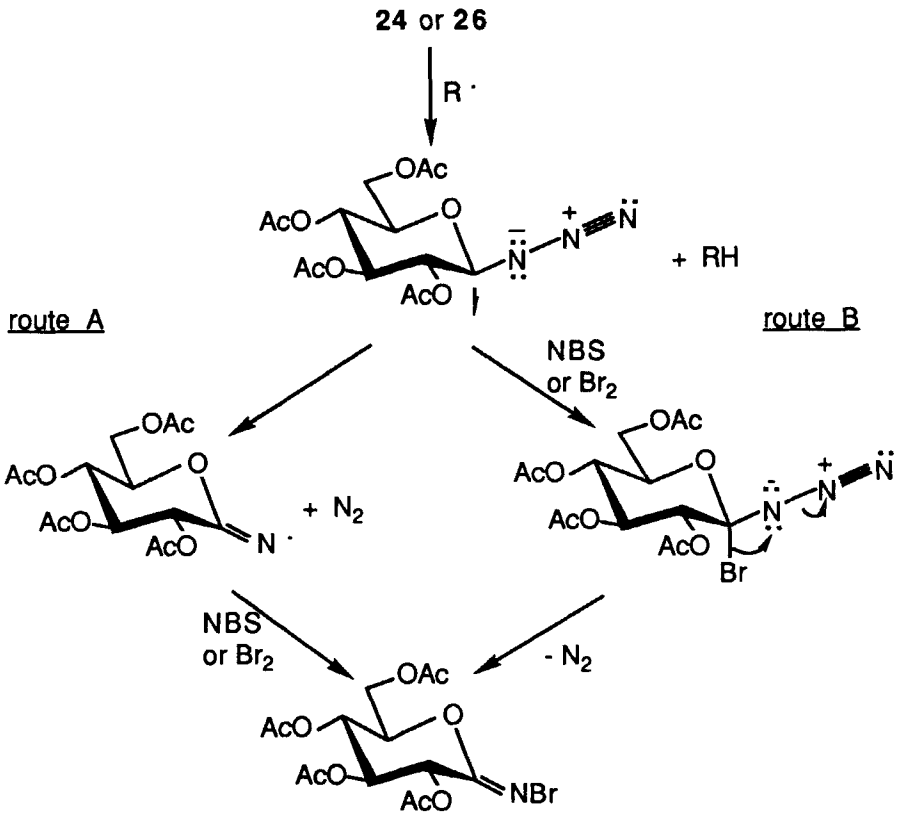
Similar conditions (SO_2Cl_2, AIBN, Δ) also brought about the transformation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide **24**[19] into the C-5 chlorinated derivative **25** (55 %) within 3-4 h. In contrast, use of NBS in boiling carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide (method A) resulted in the very fast transformation (4-6 mn) of the starting β-azide **24**. The presence of a single new spot, slightly less mobile than **24** and strongly UV light absorbing on a TLC plate, indicated a clean reaction which also occurred when the mixture was irradiated with a 250 W sun lamp (method B), in the absence of benzoyl peroxide. Though the product decomposed during attempted chromatographic purifications, it has been obtained in a pure form (92 % isolated yield) using the photolytic procedure (method B) and identified as being the new peracetylated bromimino lactone **27**.[20]

Use of molecular bromine instead of NBS does not provide alternative conditions for the preparation of **27** from **24**. However, TLC monitoring showed that the aforementioned transformation occurred within 2-3 h with the less reactive α-anomer **26**.[21] No reaction was observed either for compound **28**[22] when submitted to the same treatment or for **24** when heated in the absence of radical initiators (light or benzoyl peroxide). Recent synthetic results also demonstrate that NBS itself does not alter azide groups.[23]

The observed reactivities of the anomeric azides (β > α) suggest a free-radical abstraction of the anomeric hydrogen atom, as the initial step of the reaction, in connection with the easier homolysis of axially oriented acetalic C-H bonds, as compared to the equatorial ones.[24] This proposal is also in keeping with the stability of **28**. The suggested initial homolysis of the anomeric C-H bond which calls to mind the observed hydrogen abstraction from the α-methylene of n-butyl azide by t-butoxyl radicals[25] should benefit from the specific features of the anomeric centre[3,26] and from the acetoxy group at C-2.[27] Whereas photolysis of the azide group proceeds through other ways,[28,29] carbon-centered radicals bearing an azido substituent are involved in a few synthetic transformations.[30a] However, in the present case, decomposition of the initial radical into a lactone iminyl radical with release of molecular nitrogen should ensue, following a behaviour also encountered for alkyl azides.[25,31] The radical chain should be continued by a final bromine abstraction from either NBS or the *in situ* generated bromine.[32] Hence, despite the absence of related literature data[34] and of a unique pattern for the free radical reactivity of organic azides, route A (SCHEME 3) best represents the probable reaction pathway.

The possible bromination of the initial azido alkoxy radical (route B) constitutes a less probable alternative. The variety of resonance forms of such a radical should result in a lowered reactivity.[26] In addition, the eventual bromoazido intermediate should be, in

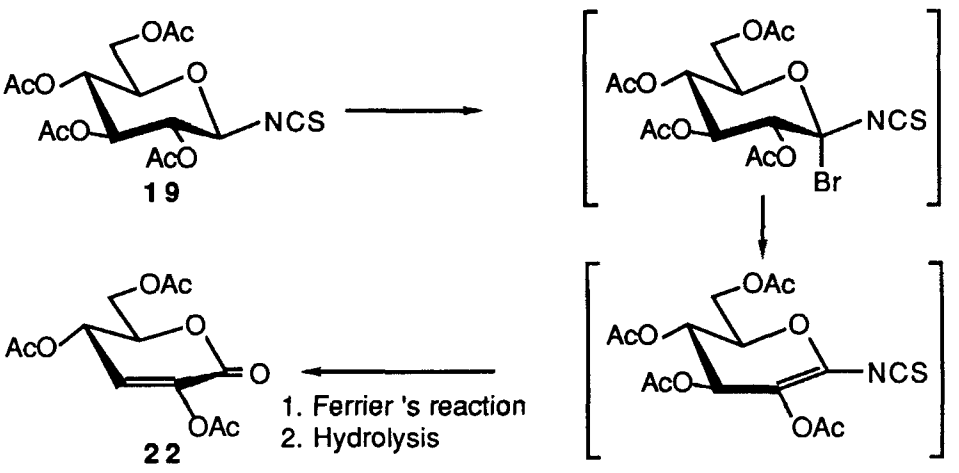
SCHEME 3



light of theoretical data,[35] a short-lived species, prone to a C-Br bond heterolysis. Since derivative **28** failed to react when exposed to the same reaction conditions, a plausible rationale for the formation of **27** via a bromoazido intermediate is not straightforward.

In contrast to the azido group, the influence of an isothiocyanate substituent towards hydrogen abstraction is better appreciated through a variety of experimental studies.[30b,36,37] An initial homolysis of the axial C-H bond most probably initiates successive transformations of the β-isothiocyanate **19**. Not surprisingly, the corresponding C-1 α-bromo adduct (SCHEME 4) remained elusive, since the stability of α-bromo isocyanate derivatives is enhanced by electron withdrawing substituents.[36] Then, a dehydrobromination step should lead to a 1,2-unsaturated compound prone to Ferrier's reaction while the final conversion to the unsaturated lactone **22** could arise from hydrolysis. Such a reaction pathway is reminiscent of the mechanism proposed for

SCHEME 4



the photohalogenation of the peracetylated phenyl-1-thio-β-D-glucopyranoside.[38] The similarity includes the action of molecular bromine which most probably favours a competitive heterolysis of the C-N glycosidic bond to yield the α-bromine **20**, as also observed in the case of β-D-thiophenyl glucosides[39] (in the absence of light) and corresponding sulfoxides.[38]

In conclusion, the studied series of sugar derivatives displaying a C-N-glycosidic bond gives rise to a variety of transformations depending on the substrate structure. While halogenation takes place essentially at the aromatic ring, with a moderate selectivity in the case of aryl-*N*-glucosides, peracetylated glucopyranosyl azides or isothiocyanate undergo in the presence of NBS (light or peroxide) an initial homolysis of the anomeric C-H bond (axial bonds more reactive than equatorial ones) which trigger further modifications of the substrate. Particularly noteworthy is the up-to-now unknown bromiminolactone generated under these conditions from a β-azide. Hence, this approach constitutes a mild, efficient and extremely simple route towards potentially interesting compounds whose reactivity and synthetic applications are under investigation.

EXPERIMENTAL

Free-radical halogenations : *in the presence of NBS*.- A suspension of NBS (2 mmol) in carbon tetrachloride (10-20 mL) containing the substrate (0.5 mmol) is boiled in

the presence of a catalytic amount of benzoyl peroxide or azoisobutyronitrile (method A) or irradiated with a 250 W tungsten lamp placed under the flask (method B). For compounds **1-17** (method A), 1-2 molar equivalents of NBS were used . *In the presence of bromine*.- A solution of bromine (1.25 mmol) and the substrate (0.5 mmol) in carbon tetrachloride (10 mL) is boiled (initiators , method C) or irradiated with either a 250 W tungsten lamp (reaction temperature 77 °C, method D) or a 450 W medium pressure mercury lamp (reaction temperature : 30-40 °C, method E). *In the presence of sulfuryl chloride*.- A solution of sulfuryl choride (2 mmol) and the substrate (0.5 mmol) in carbon tetrachloride (5 mL) is boiled in the presence of azoisobutyronitrile (method F).

After work-up, the resulting products are separated either by crystallization from diethyl ether-hexane or column chromatography (Kieselgel 60 Merck) with the following systems : benzene-diethyl ether-hexane 6/3/1 (**9-18**) or ethyl acetate-hexane 3/7 (**23, 24, 26**). Reaction times, physical and NMR data are collected in TABLES 1, 2 and 3 respectively.

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