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A Facile and Expeditious Entry to Acyclic Carbohydrate-Derived 1,2-Diazabutadienes

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Abstract: Chiral 1,2-diaza-1,3-butadienes derived from acyclic monosaccharides are easily prepared from the corresponding and readily available unprotected sugars in a two-step sequence.

Introduction

There has been an increasing interest in the chemistry of azadienes as potential progenitors for cycloaddition reactions and other synthetic transformations.[1] Chiral monoazadienes have also been successfully employed in some elegant natural product syntheses, though processes often involve lengthy and multistep sequences.[1,2] In this strategy, such chirons can serve either as chiral auxiliaries or as building blocks that are incorporated into the target molecule. Likewise, related substances such as chiral 2-amino-1,3-butadienes have recently emerged as versatile chiral auxiliaries in Diels-Alder reactions for the construction of five-, six-, and even seven-membered rings of high enantiomeric purity.[3]

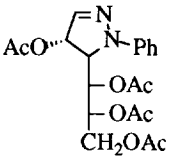
In stark contrast, the use of other hetero- and poly-azadienes remains a rather unexplored domain.[4,5] In particular, the attractiveness of 1,2-diazadienes rests on two salient applications. On the one hand their potential use as hetero-dienes or -dienophiles in cycloadditive processes, and on the other the achievement of nucleophilic 1,4-additions by exploiting the umpolung reactivity at the α-carbon, opposite to the typical electrophilic attack to carbanions derived from carbonyl compounds. Despite these promising perspectives, asymmetric transformations with these compounds have been hampered by the difficulty in preparing chiral, functionalized 1,2-diazadienes.[6]

In following our current work on asymmetric synthesis from carbohydrates, we report herein a general

synthesis of sugar 1,2-diaza-1,3-butadienes (**11**-**17** and **20**). In a previous communication, we have described the hetero-Diels-Alder reactions of a few of such diazadienes derived from D-mannose.[7] However, we sought to prepare and expand the process to other sugars in order to generalize a synthetic approach to heterocycles having functionally different carbon side chains of known and controllable absolute stereochemistry. The ready availability of sugar epimers provides both practicality and versatility in this approach toward stereochemically defined chirons. Moreover, unequivocal structural and stereochemical elucidation of sugar 1,2-diazabutadienes have now been demonstrated.

Results and discussion

Diazabutadiene Synthesis. Although the first derivative (**11**) of this class of compounds was serendipitiously prepared in the early forties by acetylating D-mannose phenylhydrazone,[8] the synthesis was rather capricious and only a few attempts were accomplished to extend the reaction to other chiral 1,2-diazadienes derived from acyclic monosaccharides. It should be pointed out that Wolfrom and Blair described initially the compound **11** as a pyrazoline derivative (**1**).[8]



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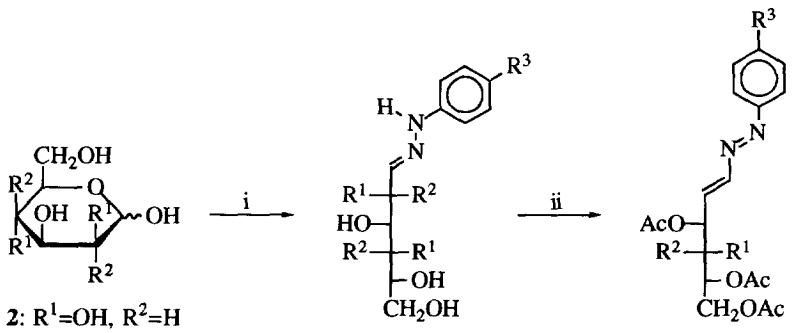
This surmise was confirmed later by Mester and Major in view of the negative formazane test for **11**, which evidenced the absence of hydrazone moiety.[9] The definitive structure of **11** was established by Wolfrom on the basis of ^{1}H-NMR studies.[10]

Likewise, aryl azoalkenes have been proposed as transient intermediates in the syntheses of aryl hydrazones and osazones. Furthermore, some reductive reactions of sugar hydrazones seem to occur through 1,2-diazadienes.[11] A plausible evidence for the intermediacy of the elusive diazadienes in such processes arises from the fragmentation pattern of acetylated sugar hydrazones in their mass spectra.[12]

Having these premises in mind, we have developed a general synthesis of sugar 1,2-diaza-1,3-butadienes in this laboratory. Thus, by treatment of D-mannose (**2**) with aryl hydrazines, the corresponding aryl hydrazones (**4**-**10**) were readily obtained. Further conventional acetylation and thermal 1,4-elimination gave 1-aryl-1,2-diaza-1,3-butadienes (**11**-**15**) in good overall yield (Scheme 1). Attempts to prepare the 4-nitrophenyl derivative were unsuccessful[13]. Starting from D-galactose (**3**), compounds **16** and **17** having D-*lyxo* configuration were similarly prepared. Alternatively, compound **11** was synthesized using the procedure by Wolfrom and co-workers[8] with slight modifications. Thus, acetylation and elimination were carried out in a single step by heating at 80°C the reaction mixture of unprotected aryl hydrazone with acetic anhydride and pyridine. In all cases, aryl diazabutadienes were colored crystalline compounds and could be stored for long times without appreciable decomposition.



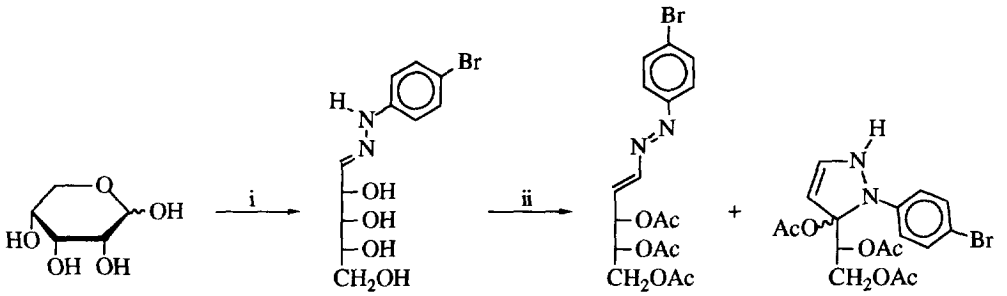
2: R^1=OH, R^2=H
3: R^1=H, R^2=OH

4: R^1=OH, R^2=R^3=H
5: R^1=OH, R^2=H, R^3=Br
6: R^1=OH, R^2=H, R^3=Cl
7: R^1=OH, R^2=H, R^3=CH_3
8: R^1=OH, R^2=H, R^3=CH_3O
9: R^1= R^3=H, R^2=OH
10: R^1=H, R^2=OH, R^3=CH_3

11: R^1=OAc, R^2=R^3=H
12: R^1=OAc, R^2=H, R^3=Br
13: R^1=OAc, R^2=H, R^3=Cl
14: R^1=OAc, R^2=H, R^3=CH_3
15: R^1=OAc, R^2=H, R^3=CH_3O
16: R^1= R^3=H, R^2=OAc
17: R^1=H, R^2=OAc, R^3=CH_3

Scheme 1. *Reagents and conditions:* i, $R^3C_6H_4NHNH_2$, <30°C; ii, Ac_2O, C_6H_5N, 60°C.

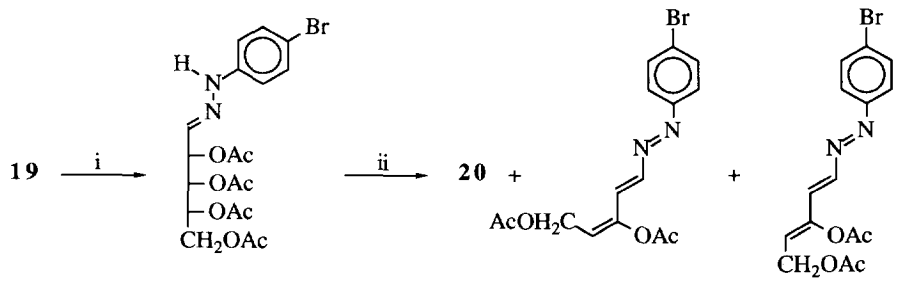
The application of the foregoing protocol to D-ribose (**18**) yielded diazabutadiene **20** along with pyrazoline **21** separable by column chromatography (Scheme 2). It should be noted the close analogy between the structure of pyrazoline **21** and that of **1**, proposed initially by Wolfrom and Blair for **11**.[8]



18 **19** **20** **21**

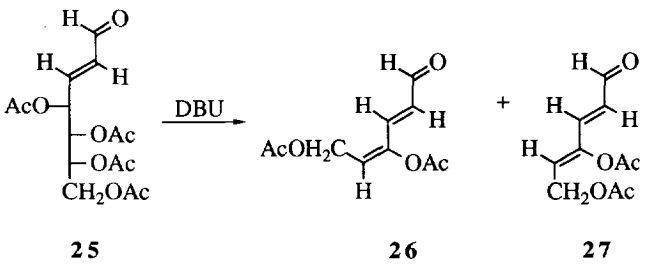
Scheme 2. *Reagents and conditions:* i, 4-Br$C_6H_4NHNH_2$, <30°C; ii, Ac_2O, C_6H_5N, 60°C

A further approach to **20** was accomplished in three steps by hydrazonation of D-ribose, which gave **19**, followed by acetylation (**22**) and elimination with DBU (1,8-diazabicycle[5.4.0]undec-7-ene) (Scheme 3). The latter step afforded not only the desired 1,2-diazabutadiene **20** but also the interesting isomeric diazahexatrienes **23** and **24**, which could be separated by column chromatography and allowed us to obtain NMR spectra of both isomers. The isomeric ratio (**24**:**23**, 85:15) was calculated from integrated ^{1}H-NMR spectra of crude products. This ratio, however, should be taken with caution since **23** in solution converts slowly into **24** as evidenced by NMR monitoring.



Scheme 3. *Reagents and conditions:* i, Ac_2O, C_6H_5N, 0°C; ii, DBU, C_6H_6, 25°C.

Analogous results have been previously reported in the reaction of acyclic α,β-unsaturated aldehydosugars with DBU[14] (Scheme 4).



Scheme 4

The process has been interpreted assuming that reaction occurs by an $E1cB_I$ mechanism[15] because of compound **26** should arise from an *anti* elimination of acetic acid, whereas a *syn* elimination would afford **27**. Nevertheless, our finding that compound **23** was transformed into **24** does not allow to rule out an E2 mechanism, leading initially to the formation of triene **23** which further isomerizes to the thermodynamically more stable product **24**.

Structural and Stereochemical Assignments. The structures of **11**-**17** were assigned on the basis of their spectroscopic data and elemental analyses. IR spectra do not display the typical NH peak at ~3300 cm^{-1}, which rules out the structure of hydrazone. Likewise, UV absorption of these substances at ~310 nm is also found in simple aryl diazabutadienes.[10,16] The alkene moiety is largely evidenced by chemical shifts and analysis of *J*-values in their ^1H NMR spectra (Tables 1 and 2). Thus, H-1 and H-2* split into double doublets at downfield chemical shifts, ~7.3 and ~6.8 ppm, respectively, which are characteristic of alkenes. The value of 13.5 Hz for $J_{1,2}$ implies a *trans* relationship for these two protons, evidencing the formation of *E*-isomers in all cases.[17,18] The formation of both *Z*- and *E*-isomers has been also documented in the literature, but the former converts into the more stable *E*-isomer.[5j] Similarly, it should be assumed that the N=N group adopts the *E*

*The original numbering of starting sugars **2**, **3**, and **18** is maintained in the related azadienes to clarify the exposition. The correct nomenclature is given in the Experimental.

Table 1. ^{1}H-NMR ($CDCl_3$): Chemical shifts (δ) of compounds **11-17**, **20**, **23**, and **24**.

Comp.	H-1	H-2	H-3	H-4	H-5	H-5'	H-6	H-6'	Ar	Me	OAc
11	7.34dd	6.79dd	5.94ddd	5.54dd	5.29ddd		4.31dd	4.21dd	7.76m, 7.46m[b]		2.15s, 2,09s
12	7.33dd	6.81dd	5.93ddd	5.54dd	5.29ddd		4.32dd	4.21dd	7.62dd		2.08s, 2.07s 2.15s, 2.10s[c]
13	7.32dd	6.80dd	5.94ddd	5.54dd	5.30ddd		4.31dd	4.21dd	7.72d, 7.43d		2.08s 2.14s, 2.09s[c]
14	7.32dd	6.74dd	5.95ddd	5.53dd	5.29ddd		4.31dd	4.20dd	7.68d, 7.26d	2.40s	2.07s 2.14s, 2.09s
15	7.31dd	6.67dd	5.91ddd	5.52dd	5.29ddd		4.31dd	4.20dd	7.76d, 6.96d	3.85s	2.08s, 2.07s 2.14s, 2.09s[c]
16	7.39d	6.80dd	5.37t	——5.52-5.45m——			4.31dd	4.04dd	7.78m, 7.46m[b]		2.07s 2.11s, 2.10s
17	7.38d	6.75dd	5.72t	——5.52-5.47m——			4.30dd	4.04dd	7.68d, 7.25d	2.38s	2.09s, 2.06s 2.10s, 2.09s
20	7.38dd	6.88dd	5.87ddd	5.39ddd	4.35dd	4.26dd			7.29m		2.08s, 2.05s 2.14s, 2.11s
23	7.29d	7.40d		5.79t	——4.90d[a]——				7.62m		2.07s 2.76s, 2.11s
24	7.23d	7.37d		5.96t	——4.67d[a]——				7.62m		2.32s, 2.09s

[a,b,c] Signals of 2, 3, and 6 protons, respectively.

Table 2. ^{1}H-NMR ($CDCl_3$): Coupling constants (Hz) of compounds **11-17**, **20**, **23**, and **24**.

Comp.	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
11	13.5	1.3	5.8	3.2	8.5			2.8	4.7	12.5
12	13.5	1.3	5.8	3.2	8.5			2.8	4.7	12.5
13	13.5	1.4	5.8	3.2	8.5			2.8	4.6	12.5
14	13.6	1.3	5.9	3.3	8.5			2.9	4.7	12.5
15	13.6	1.3	6.1	3.3	8.4			2.9	4.7	12.5
16	13.6	a	7.7	7.3	a			4.9	6.4	11.7
17	13.6	0.7	7.7	7.5	a			4.9	6.4	11.7
20	13.6	1.2	6.7	4.7	4.1	6.4	12.1			
23	13.3				7.9	7.9				
24	13.3				7.0	7.0				

[a] Not observed.

configuration, as *Z*-isomers are unstable and transform into the former.[5c] Moreover, the chemical shift of H-2 disagrees with the *Z*-isomer for the N=N bond.[17] In addition, the structure of **14** was confirmed by X-ray crystallographic analysis and shows that both double bonds exist in the *E*-configuration in the solid state.[19]

Double irradiation experiments were used to assign the remaining protons in the ^{1}H NMR spectra. In all cases the sequence $\delta_{H-1} > \delta_{H-2} > \delta_{H-3} > \delta_{H-4} > \delta_{H-5} > \delta_{H-5'}$ or $\delta_{H-5} > \delta_{H-6} > \delta_{H-6'}$ could be established. The signals are double doublets with the exception of H-3 and H-4 in **20** and H-3 and H-5 in compounds **11-17**, which present three coupling constants each. Furthermore, H-3 exhibits an allylic coupling pattern in all cases, whereas H-4 in **20** and H-5 in **11-17** show the typical signal of the proton near to terminal methylenes of sugar chains. The ^{13}C NMR spectra of **11-17** and **20** also support the structure of 1,2-diaza-1,3-butadienes (Table 3). The resonances at ~150 and ~136 ppm appear in the expected range for olefinic carbons. On the other hand, proton-decoupled DEPT experiments and comparison with model compounds allowed to assign unequivocally all carbon signals.

Table 3. ^{13}C-NMR chemical shifts (δ) of compounds **11-17**, **20**, and **24**[a,b].

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	Me
11	149.58	136.24	69.60	68.95	67.96	61.40	
12	149.87	137.15	70.02	69.34	68.37	61.77	
13	149.87	137.25	69.98	69.33	68.35	61.76	
14	150.15	135.52	70.09	69.40	68.42	61.80	21.46
15	150.22	134.26	70.18	69.47	68.47	61.81	55.53
16	151.00	135.75	70.63	68.92	67.96	61.65	
17	150.19	134.75	70.53	68.86	67.85	61.54	21.15
20	150.32	136.51	71.23	70.01	61.53		
24	146.86	135.70	146.72	122.25	58.82		

[a]In $CDCl_3$. [b]Signals of acetate groups in Experimental.

The structural elucidation of diazatrienes **23** and **24** is based on ^{1}H-NMR data: both compounds exhibit only two signals attributable to acetate groups. One of them occupies the adjacent site to the terminal methylene group, while the other lies on C-3. The location of the latter was deduced by double irradiation experiments. Also ^{13}C NMR spectra was used to confirm such structures: the chemical shifts of C-1 to C-4 ($\delta_c > 120$ ppm) are consistent with typical values for olefinic carbons and, again only two ester carbons could be detected. The major isomer obtained (**24**) was that having *Z*-configuration at C-5-C-6 double bond, whereas the minor isomer (**23**) had *E*-configuration. These assignments were based on NOE measurements as depicted in Figure 1.

The high resolution mass spectra are in accord with the structures of **20**, **23**, and **24**. In addition, mass

spectra provide further evidence on the role of sugar azoalkenes as intermediates in numerous carbohydrate transformations. Compounds **11**-**17** and **20** display the same fragmentation pattern than those of acylated sugar hydrazones.[12] These results are consistent with previous studies in which diazabutadienes were suggested as the first fragmentation products of hydrazones (Scheme 5).

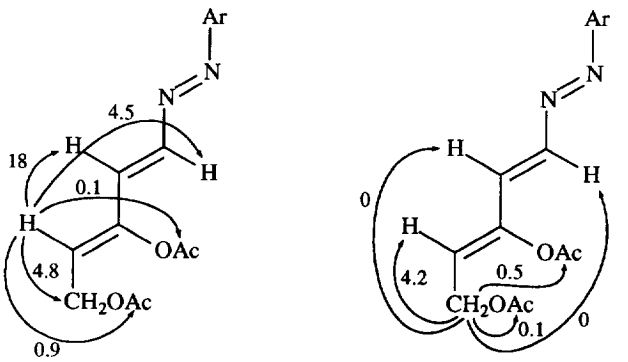
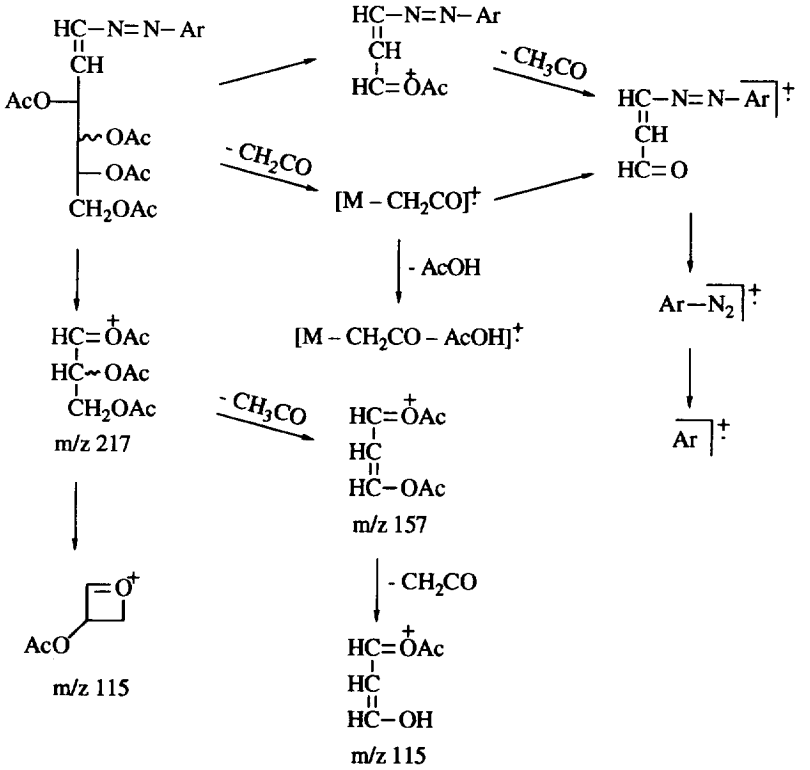


Figure 1. NOE measurements for major compound **24**



Scheme 5. Mass spectra fragmentation of aryl azoalkenes

Concluding comments

There are obvious reasons for exploring the chemistry of these unknown 1,2-diazadienes derived from acyclic monosaccharides as potential chiral auxiliaries or synthetic chirons. Thus, cycloaddition reactions would provide polyhydroxyalkyl heterocycles, which are precursors of *C*-nucleosides. As mentioned, we have already reported our preliminary experiments on [4+2] hetero-Diels-Alder reactions with these heterodienes having *D-arabino* configuration on the sugar chain. This generalized synthesis will allow to study both the regio- and diastereo-facial selectivity provided by stereochemically different sugar chains. On the other hand, nucleophilic 1,4-additions should afford functionalized carbohydrates at C-2, such as 2-deoxy- or 2-amino-sugars.

In summary, we have described a simple and efficient synthesis of chiral 1,2-diaza-1,3-butadienes, which are otherwise readily accessible from unprotected sugars, the inexpensive source of chiral pool. It is hoped that this route will encounter rapid applications in synthesis.

Experimental

All solvents employed as reaction media were reagent grade (Aldrich) and were stored over molecular sieves (4Å). Melting points were determined on a Electrothermal 8100 capillary apparatus and are uncorrected. Electronic absorption spectra were recorded on a Milton Roy Spectronic 120 spectrophotometer. Optical rotations were determined in $CHCl_3$ on a Perkin-Elmer 241 polarimeter at 15°C. IR spectra were recorded on a Perkin-Elmer 399 or a FT-IR Midac spectrophotometer using KBr pellets, unless otherwise specified. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AC-200-E or a Bruker AC-400-PC spectrometer. Chemical shifts (δ) are reported in ppm of the applied field and apparent coupling constants (J) in Hz. TMS was used as internal standard (δ_H and δ_C = 0.00) for ^1H and ^{13}C nuclei, respectively. Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with silica gel 60 F_{254} (Aldrich) of 0.25 mm thickness were used. Merck silica gel 60 (230-400 ASTM mesh) was employed for column chromatography. Combustion microanalyses were performed on a Perkin-Elmer 240C analyser. Electron impact (EI) mass spectra (35 and 70 eV) were obtained with a Kratos MS-80 RFA instrument, with a ionizing current of 100 μA, and accelerating voltage of 4 KV, and a resolution of 1000 (10% valley definition). The elemental composition of the ions was determined with a resolution of 10000 (10% valley definition).

General procedure for the preparation of (1*E*, 3*E*)-4-(tetra-*O*-acetyl-tetritol-1-yl)-1-aryl-1,2-diaza-1,3-butadienes (11-17). To a suspension of D-aldose aryl hydrazone (20.0 mmol) in pyridine (30.0 mL) was added acetic anhydride (20.0 mL) and the mixture was heated at 80°C until complete dissolution of reagents, and then for 15 min. The resulting reddish solution was cooled to room temperature and poured into ice-water (500 mL) with stirring. The solvent was decanted and the residue was dissolved in hot ethanol (50 mL). To this solution, pyridine (7 mL) and water (35 mL) were added, and the reaction mixture was heated at 100°C (external bath) for 15 min. The title product was collected by filtration and recrystallized from ethanol-water.

According to this general protocol cited above, the following 1,2-diaza-1,3-butadienes were prepared.

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-1-phenyl-1,2-diaza-1,3-butadiene (11). Prepared from D-mannose phenyl hydrazone (**4**)[20] in 46% yield. M.p. 121-123°C (lit.[10] 122-124°C); $[\alpha]_D$ -0.5 , $[\alpha]_{578}$ -1 , $[\alpha]_{546}$ -5.5 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 303, 228 nm (ε_{mM} 4.6, 2.3); IR: ν_{max} 1725 (C=O), 1615 (C=C), 1565, 1445, 1420, 1355, 1200 (C-O-C), 750 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.05, 169.31, 169.23, 169.12, 151.92, 131.04, 128.71, 122.51, 20.40, 20.31, 20.20. MS: m/z(%): 420(19), 378(5), 361(1), 318(2), 217(2), 216(5), 215(5), 203(13), 199(12), 198(24), 173(24), 162(19), 161(100), 160(12), 157(27), 145(25), 105(12), 93(19), 77(56), 60(15), 44(27).

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-1-(4-bromophenyl)-1,2-diaza-1,3-butadiene (12). Prepared from D-mannose (4-bromophenyl) hydrazone (**5**)[21] in 40% yield. M.p. 141-143°C (lit.[10] 141-142°C); $[\alpha]_D$ -8.5 , $[\alpha]_{578}$ -9.5 , $[\alpha]_{546}$ -13.5 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 318, 234 nm (ε_{mM} 5.9, 2.5); IR: ν_{max} 1760 (C=O), 1650 (C=C), 1590, 1490, 1425, 1390, 1230 (C-O-C), 840 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.45, 169.70, 169.62, 169.52, 150.88, 137.31, 129.33, 124.15, 20.77, 20.67, 20.57. MS: m/z(%): 500(21), 498(21), 458(4), 456(5), 398(2), 396(2), 278(27), 276(25), 253(23), 251(25), 241(67), 239(68), 237(42), 235(42), 225(17), 223(17), 185(9), 183(9), 173(19), 171(22), 157(34), 155(35), 115(26), 76(16), 60(58), 45(75), 44(100).

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-1-(4-chlorophenyl)-1,2-diaza-1,3-butadiene (13). Prepared from D-mannose (4-chlorophenyl) hydrazone (**6**)[22] in 38% yield. M.p. 135-136°C; $[\alpha]_D$ -9 , $[\alpha]_{578}$ -9.5 , $[\alpha]_{546}$ -13.5 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 314, 234 nm (ε_{mM} 1.5, 0.6); IR: ν_{max} 1730 (C=O), 1625 (C=C), 1570, 1560, 1465, 1355, 1210 (C-O-C), 825 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.44, 169.69, 169.61, 169.51, 151.01, 132.31, 125.83, 124.35, 20.79, 20.66, 20.57. MS: m/z(%): 456(10), 454(26), 414(2), 412(5), 239(6), 237(15), 234(14), 233(17), 232(33), 209(12), 207(31), 197(36), 196(27), 195(100), 191(44), 181(10), 179(25), 141(6), 139(13), 129(9), 127(27), 115(22), 111(48), 75(13), 60(34), 45(43). Calcd. for $C_{20}H_{23}N_2O_8Cl$: C, 52.81; H, 5.10; N. 6.16. Found: C, 53.18; H, 5.17; N, 6.17.

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-1-(4-methylphenyl)-1,2-diaza-1,3-butadiene (14). Prepared from D-mannose (4-methylphenyl) hydrazone (**7**)[22] in 38% yield. M.p. 142-143°C; $[\alpha]_D$ -13 , $[\alpha]_{578}$ -13.5 , $[\alpha]_{546}$ -18.5 (*c* 0.9, $CHCl_3$); UV (96% EtOH): λ_{max} 317, 236 nm (ε_{mM} 2.3, 1.0); IR: ν_{max} 1725 (C=O), 1630 (C=C), 1585, 1485, 1440, 1355, 1210 (C-O-C), 810 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.47, 169.72, 169.63, 169.53, 150.48, 142.06, 129.74, 122.90, 20.78, 20.70, 20.66, 20.57. MS: m/z(%): 434(30), 392(8), 375(1), 332(2), 230(4), 229(4), 217(9), 213(12), 212(21), 187(27), 176(19), 175(100), 171(31), 159(23), 119(10), 115(9), 107(18), 106(24), 91(68), 60(16). Calcd. for $C_{21}H_{26}N_2O_8$: C, 58.06; H, 6.03; N. 6.45. Found: C, 58.03; H, 6.07; N, 6.45.

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*arabino*-tetritol-1-yl)-1-(4-methoxyphenyl)-1,2-diaza-1,3-butadiene (15). Prepared from D-mannose (4-methoxyphenyl) hydrazone (**8**)[23] in 46% yield. M.p. 122-124°C; $[\alpha]_D$ -20.5 , $[\alpha]_{578}$ -23 , $[\alpha]_{546}$ -34 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 338, 244 nm (ε_{mM} 4.4, 2.3); IR: ν_{max} 1740 (C=O), 1630 (C=C), 1600, 1580, 1500, 1470, 1380, 1210 (C-O-C), 835 (arom., C=C)

cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.47, 169.72, 169.64, 169.55, 162.39, 146.71, 124.84, 114.25, 20.78, 20.71, 20.66, 20.59. MS: m/z(%): 451(13), 450(55), 408(17), 390(2), 348(2), 288(3), 257(2), 229(13), 228(24), 203(34), 192(19), 191(100), 187(36), 175(23), 149(8), 135(17), 123(17), 122(36), 108(16), 107(51), 77(21), 60(19). Calcd. for $C_{21}H_{26}N_2O_9$: C, 56.00; H, 5.82; N. 6.22. Found: C, 56.00; H, 5.86; N, 6.20.

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*lyxo*-tetritol-1-yl)-1-phenyl-1,2-diaza-1,3-butadiene (16). From D-galactose phenyl hydrazone (**9**)[24] in 42% yield. M.p. 86-87°C; $[\alpha]_D$ -70.5 , $[\alpha]_{578}$ -79 , $[\alpha]_{546}$ -116 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 301, 226 (ε_{mM} 26.6, 12.6); IR: ν_{max} 1740 (C=O), 1640 (C=C), 1580, 1560, 1530, 1470, 1210 (C-O-C), 760, and 680 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 170.15, 169.75, 169.54, 169.20, 152.17, 131.35, 128.92, 122.73, 20.64, 20.51, 20.45. MS: m/z(%): 420(26), 378(9), 362(1), 361(1), 318(3), 245(3), 217(3), 216(6), 215(5), 203(15), 199(12), 198(21), 173(21), 162(20), 161(100), 160(12), 157(16), 145(22), 115(8), 105(8), 93(9), 77(19). Calcd. for $C_{20}H_{24}N_2O_8$: C, 57.14; H, 5.75; N. 6.66. Found: C, 57.11; H, 5.70; N, 6.67.

(1*E*, 3*E*)-4-(Tetra-*O*-acetyl-D-*lyxo*-tetritol-1-yl)-1-(4-methylphenyl)-1,2-diaza-1,3-butadiene (17). From D-galactose (4-methylphenyl) hydrazone (**10**)[25] in 40% yield. M.p. 102-103°C; $[\alpha]_D$ -80 , $[\alpha]_{578}$ -89 , $[\alpha]_{546}$ -131 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 316, 233 (ε_{mM} 52.0, 25.6); IR: ν_{max} 1740 (C=O), 1650 (C=C), 1600, 1495, 1430, 1375, 1215 (C-O-C), and 825 (arom., C=C) cm^{-1}; ^{13}C-NMR ($CDCl_3$): δ 169.96, 169.58, 169.39, 169.03, 150.99, 134.75, 129.46, 122.61, 20.49, 20.35, 20.30. Calcd. for $C_{21}H_{26}N_2O_8$: C, 58.06; H, 6.03; N. 6.45. Found: C, 57.94; H, 5.97; N, 6.44.

(1*E*, 3*E*)-4-(tri-*O*-acetyl-D-*erythro*-tritol-1-yl)-1-(4-bromophenyl)-1,2-diaza-1,3-butadiene (20).- This compound was prepared from D-ribose 4-bromophenyl hydrazone (**19**)[26] according to the general procedure with slight modifications in the work-up step. The ethanolic solution was cooled to room temperature and evaporated to dryness. The residue was dissolved in dichloromethane (150 mL) and washed successively with 0.5 *N* hydrochloric acid (100 mL), saturated aqueous solution of sodium hydrogencarbonate (3 x 100 mL), dried with anhydrous magnesium sulfate, and evaporated. Crude product was purified by flash chromatography (ether-petroleum ether, 5:2) to afford the corresponding 1,2-diazabutadiene (**20**) as an oil in 40% yield, along with the pyrazoline **21** (7%). $[\alpha]_D$ +78 , $[\alpha]_{578}$ +82 , $[\alpha]_{546}$ +9.2 (*c* 1.0, $CHCl_3$); UV (96% EtOH): λ_{max} 316, 232 (ε_{mM} 46.7, 22.5); IR ($CHCl_3$): 1740 (C=O), 1640 (C=C), 1590, 1580, 1570, 1480, 1365, 1220 (C-O-C), and 830 (arom., C=C); ^{13}C-NMR ($CDCl_3$): δ 170.35, 169.87, 169.37, 150.92, 132.25, 125.84, 124.22, 20.72, 20.58. MS: m/z(%): 428(15), 426(13), 386(3), 384(4), 368(3), 366(4), 326(4), 324(5), 295(12), 293(12), 283(11), 281(11), 266(61), 264(59), 253(83), 251(89), 241(87), 239(90), 237(57), 235(57), 225(31), 223(33), 185(60), 173(47), 171(56), 157(70), 155(75), 115(19), 60(100). HRMS: m/z 428.0406 and 426.0427. Calcd. for M^+ of $C_{17}H_{19}BrN_2O_6$: 428.04072 and 426.04269.

(1*E*, 3*E*, 5*E*)- and (1*E*, 3*E*, 5*Z*)-1-(4-bromophenyl)azo-3,5-diacetoxy-1,3-pentadienes (23 and 24).- To a solution of 2,3,4,5-tetra-*O*-acetyl-*aldehyde*-D-ribose 4-bromophenyl hydrazone (**22**) (2.0 g, 4.1 mmol) in benzene (12 mL) was added DBU (0.6 mL, 4.1 mmol), and the reaction mixture was kept at room temperature for 2 h. Then, the solution was evaporated and the residue dissolved in dichloromethane (15 mL).

The organic layer was washed with 0.5 *N* hydrochloric acid (15 mL), saturated aqueous solution of sodium hydrogencarbonate (3 x 10 mL), dried with anhydrous magnesium sulfate, and evaporated. The residue was purified by preparative TLC (hexane-ethyl acetate, 3:1) to afford a mixture of compounds **23** and **24** as a reddish oil (7%). UV (96% EtOH): λ_{max} 343 (ε_{mM} 16.8); ^{13}C-NMR of **24** ($CDCl_3$): δ 170.63, 167.81, 151.44, 132.39, 125.82, 124.26, 20.76, 20.42. MS: m/z(%): 368(23), 366(17), 295(30), 293(30), 266(13), 264(11), 253(96), 251(100), 185(13), 173(15), 171(17), 157(13), 155(15), 73(13), 60(26). HRMS of **23** and **24**: m/z 368.0165 and 366.0197. Calcd. for M^+ of $C_{15}H_{15}BrN_2O_4$: 368.0196 and 366.0216.

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