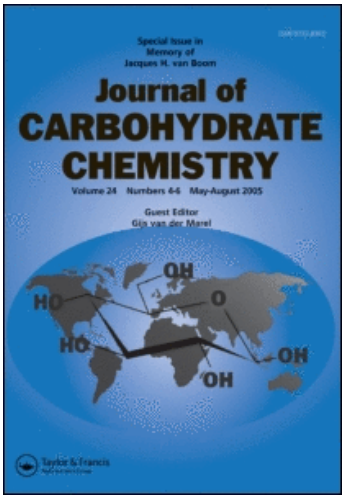

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Trans Benzoyl Migration in 1.6-Anhydro-2-azido-4-*O*-benzoyl-2-deoxy-β-D-glucopyranose in Non-Aqueous Basic Medium

Ronan Van Rijsbergen[a]; Marc Anteunis[a]; André De Bruyn[a]
[a] State University of Ghent, Laboratory of Organic Chemistry, GENT, Belgium

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COMMUNICATION

TRANS BENZOYL MIGRATION IN 1,6-ANHYDRO-2-AZIDO-4-O-BENZOYL-2-DEOXY-β-D-GLUCOPYRANOSE IN NON-AQUEOUS BASIC MEDIUM

Ronan Van Rijsbergen, Marc Anteunis and André De Bruyn*

State University of Ghent, Laboratory of Organic Chemistry
Krijgslaan 281 (S-4), B-9000 GENT (Belgium).

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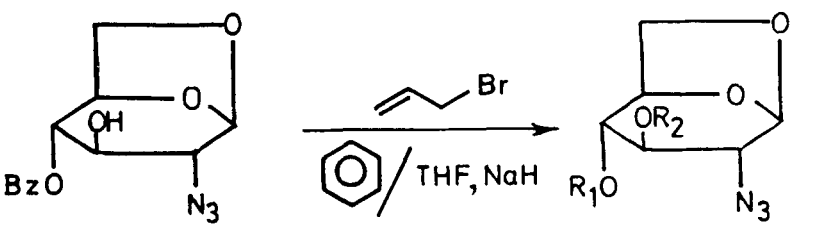
When 1,6-anhydro-2-azido-4-O-benzoyl-2-deoxy-β-D-glucopyranose[1] (1) was treated with allyl bromide in benzene-tetrahydrofuran solution in the presence of sodium hydride, we obtained the expected reaction product, 3-O-allyl-1,6-anhydro-2-azido-4-O-benzoyl-2-deoxy-β-D-glucopyranose (2), and the rearranged compounds 1,6-anhydro-2-azido-3-O-benzoyl-2-deoxy-β-D-glucopyranose (3) and 4-O-allyl-1,6-anhydro-2-azido-3-O-benzoyl-2-deoxy-β-D-glucopyranose (4).



1 2 - 4

2 R_1 = Bz, R_2 = Allyl
3 R_1 = H, R_2 = Bz
4 R_1 = Allyl, R_2 = Bz

TABLE 1 :

^{1}H NMR Data of Compounds 1-4 in $CDCl_3$ Solution (TMS Internal).

CHEMICAL SHIFTS :

	H-1	H-2	H-3	H-4	H-5	H-6A	H-6B	aromatic protons	allyl protons
1	5.51	3.30	3.96	4.84	4.67	4.19	3.67	8.01(2H), 7.48(1H), 7.38(1H)	
2	5.59	3.32	3.71	4.98	4.73	4.29	3.84	8.14(2H), 7.62(1H), 7.48(1H)	5.90(1H), 5.33(1H), 5.23(1H), 4.25(2H)
3	5.51	3.63	5.14	3.77	4.65	4.26	3.91	8.02(2H), 7.93(1H), 7.66(1H)	
4	5.59	3.34	5.26	3.42	4.43	4.13	3.91	8.02(2H), 7.61(1H), 7.58(1H)	5.98(1H), 5.37(1H), 5.24(1H), 4.37(1H), 4.27(1H)

APPROXIMATIVE COUPLING CONSTANTS* in Hz :

	$^3J_{1,2}$	$^3J_{2,3}$	$^2J_{3,4}$	$^3J_{4,5}$	$^3J_{5,6A}$	$^3J_{5,6B}$	$^2J_{6A,6B}$	$^4J_{1,3}$	$^4J_{1,5}$	$^5J_{1,6A}$	$^5J_{1,6B}$	$^4J_{2,4}$	$^5J_{2,5}$	$^4J_{3,5}$	$^5J_{1,4}$
1	1.2	1.2	1.6	1.2	0.9	5.6	7.6	2.4	0.4	0.2		0.8	0.4	1.2	0
2	1.2	1.3	1.5	1.2	0.9	5.6	7.6	2.0	0.4	0.2		1.0	0.4	1.2	0.2
3	1.0	1.7	1.8	1.2	0.9	5.6	7.6	1.4	0.4	0.2		1.0	0.4	1.6	0
4	0.9	1.8	2.0	1.3	0.8	5.8	7.5	1.4	0.3	0.2	0	1.0	0.4	1.6	0.4

* Coupling constants could not be measured first order from the ill-defined patterns of the resonances. **These values could only be obtained by comparing line widths of decoupled and** undecoupled spectral details. They should therefore only be considered as approximate values.

The structure of each product was identified by ^{1}H NMR spectroscopy[2] (see Table 1). The ^{1}H NMR data for 1 are in agreement with those reported earlier[3]. The assignment of the ring protons on C-2, C-3 and C-4 is straightforward. The position of the azido group is verified by the appearance of the H-2 resonance at the lower frequency region of the ^{1}H NMR spectra (δ 3.30-3.60). The position of the benzoyl group is ascertained by the deshielding effect of an ester grouping on its geminal proton by 1.00-2.00 ppm in comparison with the parent alcohol. In the compounds 1 and 2 H-3 is found at δ 3.96 and δ 3.71 respectively, where in 3 and 4 it is located at δ 5.14 and δ 5.26. Likewise in 1 and 2, H-4 is found at δ 4.84 and δ 4.98 respectively, but at δ 3.77 and δ 3.42 in 3 and 4.

When the poor leaving capacity of an azido group in 1 is taken into consideration, epoxide formation between C-2 and C-3 is impossible under the present reaction circumstances, but an epoxide leading to 1,6:3,4-dianhydro-2-azido-2-deoxy-β-D-galactopyranose is expected. In order to avoid this side compound, we have modified the normal procedure for allylation by adding allyl bromide prior to adding sodium hydride. No epoxide was detected. Thus, to a stirred solution of 1 (50 mg, 0.17 mmole) and allyl bromide (100 µl, 1.15 mmole) in dry benzene-tetrahydrofuran (50:50, 1 ml) an excess of sodium hydride is added in portions at -10°C. Stirring is continued for 36 hours, without further cooling. The neutralized reaction mixture (with acetic acid at -10°C) is filtered and the filtrate concentrated. The residue is dissolved in chloroform, shaken with ice cold saturated sodium hydrogen carbonate, washed with water to neutrality and dried with magnesium sulfate. Evaporation of the organic layer affords a light yellow syrup, that is chromatographed on silica gel with 2:1 hexane-ethyl acetate yielding three pure compounds (R_f values for TLC on silica gel with 3:2 hexane-ethyl acetate): 2 {R_f = 0.55, syrup, $[\alpha]_D^{20}$ -16° (c 0.61 in chloroform), yield 6 mg, Anal. Calcd for $C_{16}H_{17}O_5N_3$: C, 58.00; H, 5.17. Found C, 57.64; H 5.06}, 3 {R_f = 0.23, m.p. 151-153°C, $[\alpha]_D^{20}$ -3° (c 0.83 in chloroform), yield 10 mg, Anal.

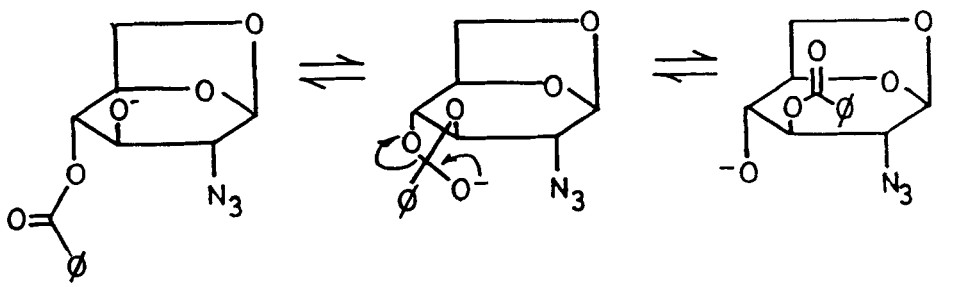


FIG. 1.

and 4 R_f = 0.47, syrup, $[\alpha]_D^{20}$ -9° (c 0.89 in chloroform), yield 13 mg, Anal. Calcd for $C_{16}H_{17}O_5N_3$: C, 58.00; H 5.17. Found C 57.72; H 5.26}.

1 was prepared in 67% yield from 1,6:2,3-dianhydro-4-O-benzoyl-β-D-mannopyranose as described by Paulsen et al.[3], except that 1.2 mole equivalent of pivalic acid was added in order to neutralize the ammonia formed during the reaction {m.p.: 92°-93°C, $[\alpha]_D^{20}$ -85.8° (c 0.92 in dichloromethane) in accordance with ref. 3}. Comparison of the present NMR data (see Table 1) with those reported by Budéšínský et al.[4] for 1,6-anhydro-β-D-aldohexopyranoses demonstrates that the reported compounds 1-4 possess a gluco-configuration, with a somewhat more flattened pyranose ring in 3 and 4 [5].

Taking into consideration the proposal of Černý and Staněk Jr.[5] that the conformation of the pyranose ring in 1,6-anhydro-β-D-aldohexopyranoses can be considered as an equilibrium mixture $^1C_4(D) \rightleftarrows B_{0,3}(D)$, a mechanism can be proposed to explain the rearranged compounds 3 and 4. In the half chair conformation the deprotonated hydroxyl group on C-3 can approach close enough to the carbonyl function of the benzoyl group for a nucleophilic attack, affording a tricyclic ortho acid anion as intermediate, from which the benzoyl group migrates easily from C-4 to C-3 (see FIG. 1).

Although it is generally accepted that the $B_{3,0}(D)$ conformation is disfavoured for steric reasons against the $^{1}C_{4}(D)$ conformation, the set of coupling constants between the ring protons of the pyranose rings (see Table 1) show that a large substituent on C-3 like the benzoate grouping may shift the usual equilibrium $^{1}C_{4}(D) \rightleftarrows B_{0,3}(D)$ towards the right side. This conformational change may imply the driving force for the rearrangment.

A similar trans rearrangment explains the behaviour of the t-butyl dimethylsilyl (TBDMS) protecting group in the study of van Boeckel et al.[6]. Moreover, the occurrence of compound 4 implies that the migration is actually a substantial part of the reaction itself and does not occur during the isolation as proposed by Černý and Staněk Jr.[5] for a similar cis rearrangment in 2-acetamido-1,6-anhydro-2-deoxy-β-D-galactopyranose derivatives[7].

ACKNOWLEDGMENT.

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REFERENCES and NOTES.

1. The benzoyl group was chosen as protective group because of its stability in non-aqueous basic circumstances; See e.g. "Protective Groups in Organic Synthesis, T.W. Green (Ed. J. Wiley & Sons), N.Y., 1981, p. 300.

2. The spectra were recorded on a Bruker WH360 spectrometer, at 18°C for 2% solutions (FT mode, pulse angle 19°, quadrature detection, resolution 0.208 Hz/point).

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