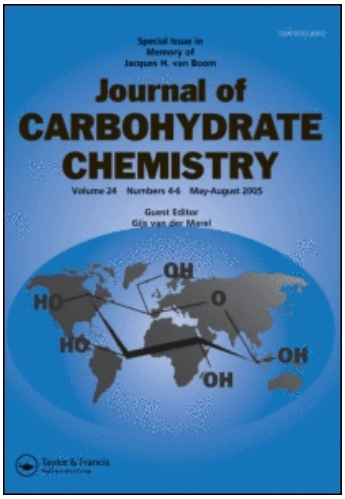

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Unusual Formation of Acetylenic Sugar from the Cyanohydrins of 1,2 : 3, 4-Di-*O*-Isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose

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UNUSUAL FORMATION OF ACETYLENIC SUGAR FROM THE CYANOHYDRINS OF 1,2:3,4-DI-O-ISOPROPYLIDENE-α-D-GALACTO-HEXODIALDO-1,5-PYRANOSE.

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ABSTRACT.

Reaction of methanesulfonate esters 3a and 3b with sodium azide in N,N-dimethylformamide gave 6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-6-heptyno-1,5-pyranose 5. The latter was identified by IR, NMR and mass spectrometry. A pathway for the unusual formation of an alkyne is proposed.

INTRODUCTION.

During the course of our studies directed towards lincosamine synthesis,[1] we tried to transform the cyanohydrins 2a and 2b into the corresponding α-azido-nitriles 4a and 4b by methanesulfonation followed by nucleophilic displacement of methanesulfonate group with azide anion.

RESULTS AND DISCUSSION.

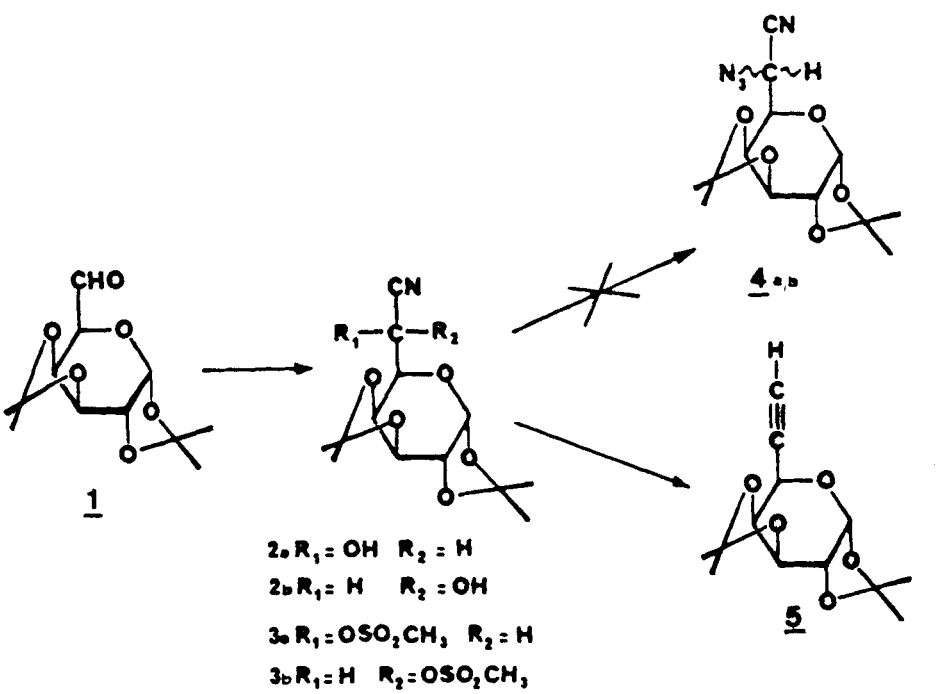
The two crystalline methanesulfonate esters[2] 3a and 3b (see experimental) were reacted with sodium azide under classical conditions (DMF, 80°C). After 36h., TLC of the reaction mixture showed a single spot less polar than the starting material. Work up

afforded a new compound which was purified by flash chromatography. The IR spectrum of this product showed no methanesulfonate ester absorption and, inter alia, a sharp band at 3280 cm^{-1} together with a weak absorption at 2140 cm^{-1} which could not be attributed to the characteristic intense peak of an azido group.

Moreover, the absence of vinylic proton in the ^1H NMR spectrum precluded the formation of an α-β unsaturated nitrile resulting from competitive elimination frequently observed with hindered sulfonic esters.[3]

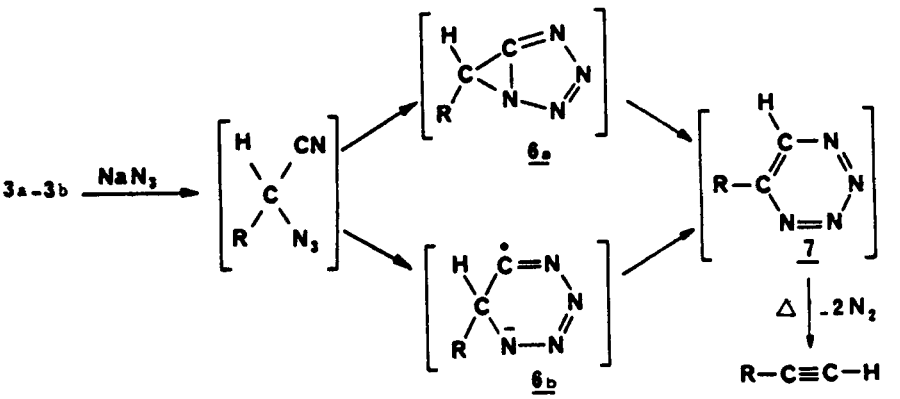
After careful examination of all analytical data it turned out that the unknown was 6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-6-heptyno-1,5-pyranose 5, which was previously prepared by Tronchet et al. in a different way.[4]

The structure was supported by elemental analysis, fitting IR spectrum and the requisite substituent resonances displayed in the ^1H NMR spectrum, significantly H-7 signal was a sharp doublet (δ 2.50 ppm, $^4J_{5,7}$= 2.5Hz). No molecular ion peak was present in the mass spectrum but the fragmentations were similar to



those previously reported,[4] and a peak of m/z 272 $(M+NH_4)^+$ was the base peak in ammonia induced chemical ionization spectrum.

Although it is too early to propose a mechanism for the formation of 5, the following sequence could be envisaged.



The intramolecular dipolar addition of alkyl or aryl azides to C≡N is well documented for γ- or δ-azido-nitriles,[5] but not known for α-azido-nitriles. In fact, to the best of our knowledge, only one α-azido-nitrile is reported, the α-azido-acetonitrile.[6]

On the other hand, strained structures similar to 6a as well as the valence isomer 6b were envisaged to explain the formation of 1,2,3-triazine (the C-analog of hypothetical 1,2,3,4-tetrazine 7) from diversely substituted α-azido-cyclopropenes.[7] Several 1,2,3-triazines were already isolated and characterized,[7,8] whereas it is understandable that the 1,2,3,4-tetrazine 7 will decompose readily to nitrogen and the isolated alkyne 5. Indeed, gas evolution was detected during the course of the reaction.

Finally, from the synthetic point of view, since the reaction can be performed with the epimeric mixture of methanesulfonate esters 3a-b, the overall yield from the aldehyde (40-45%) is comparable to that reported earlier.[4,9]

This reaction is currently under study in our laboratory because, if general, it could become a very useful way to alkynes from aldehydes, as an alternative to Corey procedure.[10]

EXPERIMENTAL

General Procedures. Melting points are uncorrected. R_F values refer to TLC performed on Merck aluminium sheets precoated with silica gel 60/PF-254 with the noted solvent systems. Column chromatography was performed with silica gel 60 (Merck, 230-400 mesh) with petroleum ether (b.p. 40-70°C)/ether. Optical rotations were determined with a Perkin-Elmer 141 polarimeter.

1,2:3,4-di-O-isopropylidene-6-O-(methylsulfonyl)-α-D-glycero-D- galacto-heptopyranuronitrile 3a and its β-L-glycero-D-galacto isomer. The dialdo-pyranose 1[11] was prepared in 70% yield by Swern oxidation[12] of 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.[13] Compound 1 was better transformed into the cyanohydrins 2a and 2b by the following two step, one-pot, procedure: aqueous sodium bisulphite (4M, 1.5 mL, 6 mmol) was poured onto 1 (1.548 g, 6 mmol) and vigorous stirring maintained 20 min. at 40°C. The resulting white precipitate was dissolved by adding ethanol (1.2 mL) and allowed to react with sodium cyanide (441 mg, 9 mmol, 1.5 equivalent) for 2 hours at 40°C. Standard work-up yielded 1.624 g (95%) of pure cyanohydrins; TLC R_F= 0.60 (pet. ether/ether 25:75) which were methanesulfonylated in the conventional way[2] to afford a 70:30 mixture of 3a and 3b (90%); TLC R_F= 0.47 and 0.53 (pet. ether/ether 25:75). The two isomers were separated by crystallization and column chromatography:

Compound 3a;	m.p. 122-123°C	$[\alpha]_D^{20}$	-92.5 (c 1.0, $CHCl_3$)
Lit.[2]	m.p. 124-125°C	$[\alpha]_D^{20}$	-98.6 (c 1.0, $CHCl_3$)
Compound 3b;	m.p. 154-156°C	$[\alpha]_D^{20}$	-46.6 (c 1.6, $CHCl_3$)
Lit.[2]	m.p. 157-159°C	$[\alpha]_D^{20}$	-46.8 (c 1.6, $CHCl_3$)

6,7-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-6-heptynо-1,5-pyranose 5. Sodium azide (49 mg, 0.75 mmol, 1.5 eqt) was added to a solution of 3a (183 mg, 0.50 mmol) in DMF (2 mL) and the resulting mixture heated for 36 hours at 80°C. Evaporation of DMF (1 torr, 50°C) and trituration of the residue in water (5 mL) followed by extraction with ether (3x15 mL) and classical work-up left a light brown oil (176 mg). Flash chromatography yielded 5

(65 mg, 51%) as a colorless oil; TLC R_F= 0.60 (pet.ether/ether 50:50); $[\alpha]_D^{20}$ -122 (c 1.4, $CHCl_3$), Litt.[4] $[\alpha]_D^{23}$ -125.9 (c 1.4, $CHCl_3$); IR (neat) 3280, 2140, 1380, 1370 cm^{-1}; ^1H NMR 80 MHz ($CHCl_3$) δ 5.54 (d, 1H, $J_{1,2}$= 5Hz, H-1), 4.60 (m, 2H, H-3 and H-5), 4.27 (m, 2H, H-2 and H-4), 2.50 (d, 1H, $J_{5,7}$= 2.5Hz, H-7), 1.52 (s, 6H, $2CH_3$), 1.36 and 1.33 (2s, 6H, $2CH_3$); MS (CI NH_3) 272 (100, $(M+NH_4)^+$), MS 239 (27, M^+-CH_3), 113(100), 100(37), 93(40), 85(50), 59(97). **Starting from the L-glycero methanesulfonate 3b** (77 mg, 0.21 mmol) the same procedure yielded 5 (23 mg, 43%).

Anal. Calcd for $C_{13}H_{18}O_5$ (254.26): C, 61.41; H, 7.14.
Found : C, 61.36; H, 7.22.

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