Conclusions

Quantitative agreement of calculation and experimental data was obtained for the first time for final depletions and maximum reaction rate in the chain explosion of a stoichiometric explosive mixture close to the first combustion limit.

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MIGRATION OF AN ACETYL GROUP IN GLUCOSAMINE AND GLUCOSE DERIVATIVES BY THE ACTION OF BUTYLLITHIUM. THE SYNTHESIS OF AN N-ACETYLGLUCOSAMINE 4-PHOSPHATE DERIVATIVE

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Phosphorylated sugars are common in nature. In particular, these compounds are found in the polysaccharides of meningococci [1], Teichoic acids [2], and lipopolysaccharides of Gram-negative bacteria [3]. Inage et al. [4] have recently proposed a new phosphorylation method, in which the sugar hydroxyl group first reacts with BuLi, and the lithium alcoholate formed reacts with a substituted chlorophosphate. This method is efficient for the introduction of phosphate at C^4 in glucosamine.

However, the phosphorylation of methyl 2-acetamido-3,4-di-O-acetyl-2-desoxy-α-D-glucopyranoside (I) unexpectedly led to the formation of two compounds containing phosphate groups. This led us to undertake a detailed study of the first reaction step. Upon the action of BuLi, (I) is converted over several minutes at −70°C to a new compound (II) (as indicated by thin-layer chromatography). Under optimal conditions using fresh BuLi, an argon atmosphere and the exclusion of moisture, 95% conversion is noted. According to PMR spectroscopy (Table 1), (II) is methyl-2-acetamido-3,6-di-O-acetyl-2-

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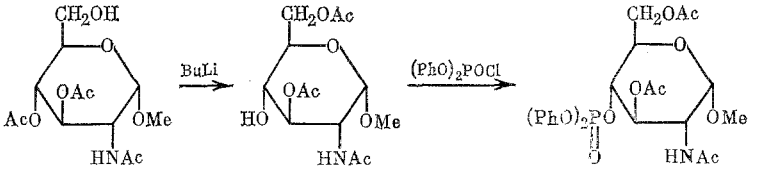
TABLE 1. Chemical Shifts (ppm) and Coupling Constants (Hz) in the PMR Spectra of α-Methylglycoside Acetates of 2-Acetamido-2-desoxy-D-glucose, D-glucose and Their Phosphorylated Derivatives

Compound	H^1 ($J_{1,2}$)	H^2 ($J_{2,3}$)	H^3 ($J_{3,4}$)	H^4 ($J_{4,5}$)	H^5 ($J_{5,6}$) ($J_{5,6'}$)	H^6 / $H^{6'}$ ($J_{6,6'}$)	NH ($J_{2,NH}$)	OCH_3	OAc	OH ($J_{H,OH}$)
(I)	4,75 d (3,8)	4,32 d.d.d. (9,7)	5,06 t (9,7)	5,27 d.d (10,5)	3,55–3,75 m		5,74 d (9,5)	3,41 s	1,97; 2,03; 2,08	3,08 d (5,5)
(II)	4,70 d (3,9)	4,26 d.d.d (10,7)	5,09 d.d (9,6)	3,61 m (9,6)	3,79 m (2,4) (4,3)	4,29 d.d / 4,52 d.d (12,0)	5,81 d (9,6)	3,41 s	1,97; 2,11; 2,16	3,09 d (5,4)
(III)	4,72 d (3,7)	4,33 m (10,6)	5,35 d.d (9,2)	4,79 q (9,2) J_{H4P}=9,2	3,79 m (2,4) (4,2)	4,11 d.d / 4,30 d.d (12,5)	5,73 d (9,7)	3,41 s	1,87; 1,96; 2,03	–
(IV)	4,66 d (3,7)	4,25 m (9,8)	5,02 t (9,8)	5,19 d.d (10,5)	3,79 m	4,20–4,37 m	5,67 d (9,4)	3,31 s	1,96; 2,01; 2,02	–
(V)	4,74 d (3,8)	4,35 d.d.d. (10,0)	5,12 t (10,0)	5,22 t (10,0)	3,92 m (2,2) (4,8)	4,11 d.d / 4,25 d.d (12,2)	5,69 d (9,7)	3,41 s	1,97; 2,03; 2,04; 2,11	–
(VI)	5,72 d (8,3)	5,06–5,18 m		5,31 t (9,5)	3,55–3,82 m		–	–	2,03; 2,04; 2,08; 2,13	– *
(VII)	5,71 d (8,2)	5,02–5,18 m		3,62 m	3,70 m (2,1) (3,9)	4,31 d.d / 4,50 d.d (12,6)	–	–	2,06; 2,10; 2,11; 2,15	– *

*Exchange of OH by OD occurred.

desoxy-α-D-glucopyranoside formed as a result of the migration of the acetyl group from C^4 to C^6 of the glucosamine, as indicated by the upfield shift of the signal for H^4 from 5.27 ppm in (I) to 3.61 ppm in (II) and its additional splitting with $J_{H,OH}$ coupling constant equal to 5.4 Hz.

The consecutive addition of BuLi and diphenyl chlorophosphate to (I) leads to an 83% yield of a 95:5 mixture of the 4- and 6-diphenylphosphates of the substituted glucosamine ((III) and (IV), respectively).



(I) (II) (III)

The structure of (III) was established by PMR spectroscopy. These spectral data are given in Table 1. The PMR spectra of the α-methylglycosides of 2-acetamido-3,4-di-O-acetyl-2-desoxy-6-O-diphenylphospho-D-glucose (IV) and 2-acetamido-3,4,6-tri-O-acetyl-2-desoxy-D-glucose (V) obtained from (I) and $(PhO)_2POCl$ in the presence of pyridine and 4-dimethylaminopyridine [5] were examined in order to study the effect of the position of the diphenylphosphate and acetate groups on the chemical shifts of the corresponding protons. Table 1 shows that the phosphorylation shifts the H^6 signal from 3.55-3.75 ppm in (I) to 4.20-4.37 ppm in (IV). The signal for H^4 in (II) at 3.61 ppm is shifted to 4.79 ppm in (II) and further splitting of this signal is noted with $J_{H^4,P}$ = 9.2 Hz. The acetylation leads to an even greater downfield shift of the signals for the protons at C^4 or C^6.

The migration of the acetyl groups at C^2, C^3, and C^4 of the monosaccharide derivatives on the adjacent hydroxyl group, especially, the 4 → 6 acyl migration, under various conditions is well known [6, 7]. However, the simplicity of the proposed methods and its high efficiency make it useful for the preparation of sugars with a free hydroxyl group at C^4. This was confirmed in the case of 1,2,3,4-tetra-O-acetyl-β-D-glucopyranose (VI). This compound was previously isomerized to 1,2,3,6-tetra-O-acetyl-β-D-glucopyranose (VII) in 20% yield in aqueous NaOH [8], while the yield of (VII) was 90% using our procedure.

Experimental

The PMR spectra were taken on a Bruker-Physik WM-250 spectrometer in $CDCl_3$ at 30°C relative to TMS. Thin-layer chromatography was carried out on Woelm silica gel plates with elution by 8:2 chloroform–acetone. The elemental analysis data of the compounds corresponded to the calculated values.

Acetyl Group Migration. A solution of the starting compound in 5 ml dry THF was cooled to −70°C and 0.3 N BuLi in pentane (1.25 eq) was added. Then, 0.02 ml acetic acid was added over 3-5 min with monitoring by thin-layer chromatography. The mixture was evaporated. The residue was dissolved in chloroform and subjected to chromatography on a silica gel column with elution by chloroform and 8:2 chloroform–acetone. The yield of the chromatographically uniform product was 90%.

A sample of 50 mg (I) with R_f 0.28, mp 96-97°C, and $[\alpha]_D^{25}$ + 95.7° ($CHCl_3$) [9] gave a syrup which crystallized upon the addition of dry ether to give 35.5 mg (71%) (II), R_f 0.32, mp 172-173°C, $[\alpha]_D^{25}$ +39.4° (C 0.2, $CHCl_3$).

A sample of 20 mg (VI) with mp 127-128°C and $[\alpha]_D^{25}$ +9.0° ($CHCl_3$) [10] gave (VII) as a syrup. The yield of (VII) was 18 mg (90%), $[\alpha]_D^{25}$ −25.8° (C 0.1, $CHCl_3$) [8] ($[\alpha]_D^{25}$ −33.0° ($CHCl_3$)).

Migration and Phosphorylation. A sample of 100 mg (I) was isomerized under the conditions described above (3 min at −60°C) and then 0.126 ml diphenyl chlorophosphate (1.5 eq) was added at this temperature. After 3 min, the solution was evaporated and the residue was dissolved in chloroform and subjected to chromatography on a silica gel column with elution by chloroform and 85:15 chloroform–acetone. The yield of the uniform product was 144 mg (83%), $[\alpha]_D^{25}$ +46.9° (C 0.4, $CHCl_3$). PMR spectroscopy indicated that this product was a 95:5 mixture of (III) and (IV).

Methyl 2-Acetamido-3,4-di-O-acetyl-2-desoxy-6-O-diphenylphosphoryl-α-D-glucoside (IV). Samples of 0.045 ml pyridine, 69 mg 4-dimethylaminopyridine (1.2 eq), and 0.253 ml diphenyl chlorophosphate (2 eq) were added consecutively to a solution of 150 mg (I) in 15 ml dry benzene. After 1 h at 20°C, the precipitate formed was separated by filtration. The solution was evaporated and the residue was subjected to chromatography on a silica gel column to give 248 mg (96%) (IV), $[\alpha]_D^{25}$ +65.6° (C 0.7, $CHCl_3$).

Methyl 2-Acetamido-3,4,6-tri-O-acetyl-2-desoxy-α-D-glucoside (V) was obtained in quantitative yield by the acetylation of 50 mg (I) using acetic anhydride in pyridine, $[\alpha]_D^{25}$ +79.9° (C 0.4, $CHCl_3$) ($[\alpha]_D^{25}$ +87.5° ($CHCl_3$) [11]).

Conclusions

The migration of the acetyl group from C^4 to C^6 occurs in partially acetylated derivatives of D-glucose and D-glucosamine upon reaction with butyllithium.

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SOME OPTICAL PROPERTIES OF DIBENZO-18-CROWN-6 DERIVATIVES

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Dibenzo-18-crown-6 diamine is a starting material for the synthesis of dibenzo-18-crown-6 (DBC) derivatives at the benzene rings, which hold interest as effective complexation agents [1].

The initial nitration of DBC in the synthesis of the amino derivatives gives a mixture of nitro derivatives consisting of 4,4'-dinitro-DBC (cis isomer) (I) and 4,5'-dinitro-DBC (trans isomer) (II) [2]. The reduction of the nitro derivatives gives 4,4'- and 4,5'-diamino-DBC, (III) and (IV), respectively.

UV, IR and PMR spectroscopy of the cis and trans isomers of dinitro- and diamino-DBC did not permit their identification [2] or determine the extent of their separation. Melting points and solubility in organic solvents are usually used for this purpose. The cis isomers have lower melting points than those of the corresponding trans isomers. These cis isomers also have higher solubility in organic solvents.

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