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Preliminary communication

Unexpected transformation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosylidene 1,1-diazide with triphenylphosphine

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Sugar phosphinimines, easily available by our method from azido sugars [1], are appropriate precursors of a number of N-containing derivatives (e.g., sugar carbodiimides, ureido sugars) [1–3]. The recent synthesis of glucopyranosylidene diazides [4] prompted the application of the phosphinimine method to this new class of azido sugars. We now report the first results of this reaction.

A solution of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosylidene 1,1-diazide (**1**, 192 mg, 0.463 mmol) [4] in dry ether (3 mL) was treated with triphenylphosphine (134 mg, 0.511 mmol). After 24 h at room temperature 6(*R*)-acetoxymethyl-7(*S*)-acetoxy-4-(triphenylphosphinimino)-6,7-dihydro-pyrano[3,4-*d*]*v*-triazole (**2**) precipitated from the mixture in 86% yield. Recrystallization from $CHCl_3$–ether gave nice white crystals of **2**, mp 199–200 °C; $[\alpha]_D$ +8° (*c* 2.3, $CHCl_3$), +17° (*c* 2, AcOH); ν_{max}(KBr) 1750 (OAc), 1613 (*v*-triazole, C=C), 729, 695 cm^{-1} (Ph); Raman (solid): 1608, 1584 (*v*-triazole, C=C), 1592, 1575, 1026, 1002 cm^{-1} (Ph); λ_{max}(EtOH) 290 nm (ϵ 29175). FABMS:

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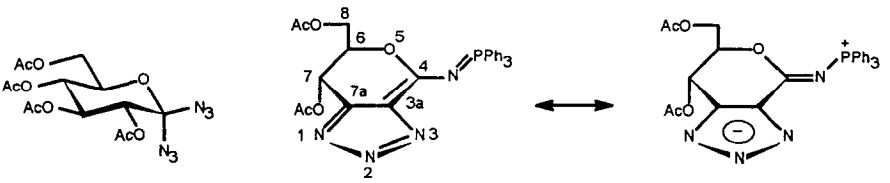


1 2

m/z 529 $[M + H]^+$. Anal. Calcd for $C_{28}H_{25}N_4O_5P$: C, 63.63; H, 4.77; N, 10.60; P, 5.86. Found: C, 63.31; H, 4.89; N, 10.31; P, 5.58.

The structure of **2** was established by NMR spectroscopy. Its ^1H NMR spectrum ($CDCl_3$, 400 MHz) showed the presence of two acetoxy groups (δ 2.063 s, 1.849 s) and that of four other nonaromatic protons (δ 6.29 d, 1 H, $J_{6,7}$ 3.6 Hz, H-7; 4.67 m, 1 H, H-6; 3.88 dd, 1 H, $J_{6,8a}$ 4.9 Hz, H-8a; 3.69 dd, 1 H, $J_{6,8b}$ 5.4 Hz, H-8b; $J_{8a,8b}$ 12.1 Hz) in the molecule.

The ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) revealed three carbon atoms at quite low field (δ 164.95, $J_{C\text{-}4,P}$ 8.1 Hz, C-4; 144.83, $J_{C\text{-}7a,P}$ 2.2 Hz, C-7a; 132.36, $J_{C\text{-}3a,P}$ 14.0 Hz, C-3a). These values correspond well to carbons of the delocalized unsaturated system including the *v*-triazole ring. Additionally, three pyranoid carbons in the usual region (δ 82.09, C-6; 63.59, C-7; 61.66, C-8) were found.

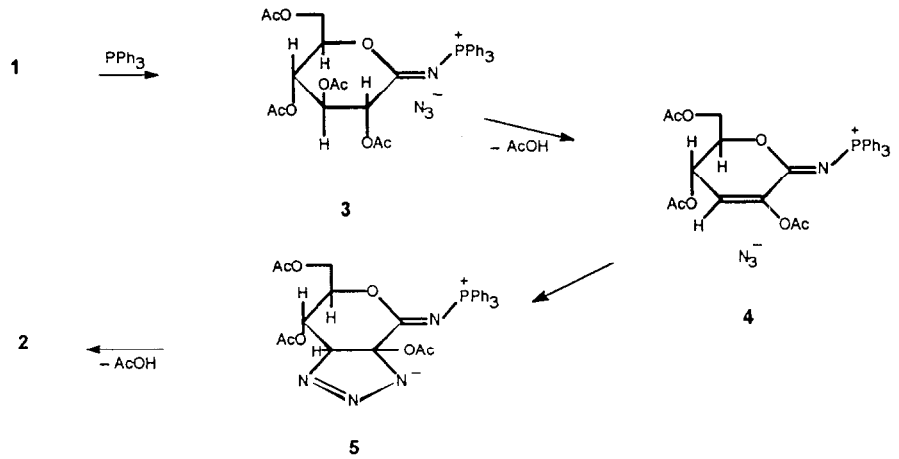
Correctness of assignments of C-6 and C-7 was proved by one-dimensional (1D) hetero-correlated experiments [5]. Signals of C-4 and C-7a were assigned by long-range correlation measurements, by selective irradiation at δ 4.67 ppm [6] and on the basis of $J_{C,P}$ coupling values. In the ^{31}P NMR spectrum, phosphorus exhibited a signal at δ 23.87 which is shifted down field with respect to the value of phosphorus in sugar phosphinimines, but is at a much higher field than that of aminophosphonium salts [2,3]. This is in good agreement with the resonance-stabilized iminophosphorane structure of **2** which was also corroborated by X-ray crystallography [7].

The mechanism of the reaction may be interpreted by the pathway presented in Scheme 1.

After the formation of the phosphinimine from one of the two azido groups, elimination of the second one as azide anion affords the ion pair **3**. Release of H-2 and subsequent β-elimination of acetate from C-3 leads to **4** in which the double bond between C-2 and C-3 is activated by the positive charge of the triphenylphosphonio moiety for nucleophilic cycloaddition of an azide anion giving **5**. During the last steps, stabilization of **5** occurs by splitting off a second molecule of AcOH to give **2**.

The probability of the cycloaddition step of this pathway from **4** to **5** can be supported by the easy formation of a *v*-triazolo-nucleoside of an analogous ring system [8] from an unsaturated pyranosyl nucleoside with cycloaddition and subsequent β-elimination.

In contrast to sugar phosphinimines, **2** does not react with carbon dioxide in acetonitrile due to its resonance-stabilized phosphinimine structure. In accordance, the



Scheme 1.

one-pot reaction of **1** with triphenylphosphine and carbon dioxide in dry toluene resulted in the isolation of **2** in excellent yield.

Studies on the reactivity of **2** and on the extension of the reaction to other diazides are in progress.

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