BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1263—1264 (1978)

Formation of (4*S*,5*R*)-4-(Nitrovinyl)-2-phenyl-1,3-dioxan-5-yl Formate from Methyl 4,6-*O*-Benzylidene-2-deoxy-2-nitro-β-D-glucopyranoside

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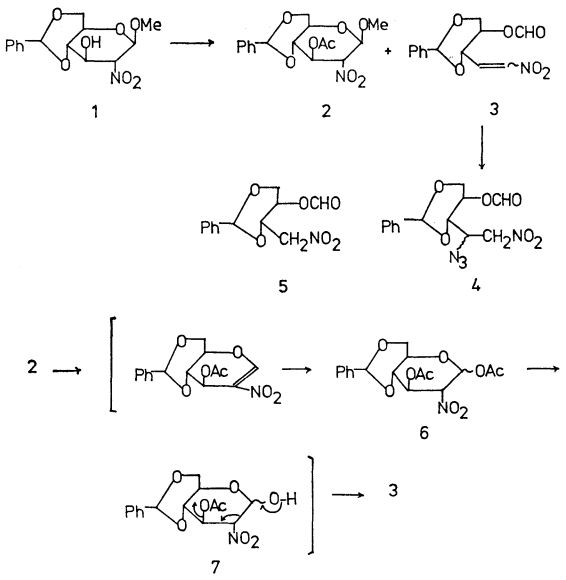
(Received September 19, 1977)

Synopsis. Acetylation of methyl 4,6-*O*-benzylidene-2-deoxy-2-nitro-β-D-glucopyranoside with acetic anhydride–pyridine afforded a mixture of the expected 3-*O*-acetate and the title compound in a *ca.* 1:1 ratio; the structure of the latter compound was confirmed by conversion into an adduct with hydrazoic acid.

Acetylation of the nitro alcohol **1** with acetic anhydride–sodium acetate gave the corresponding 3-*O*-acetate **2** in 70% yield,[1] but treatment of **1** with acetic anhydride–pyridine unexpectedly gave the title compound **3** besides the acetate **2**. In this paper we wish to report on the structural determination of **3**.

Treatment of **1** with acetic anhydride and pyridine at room temperature for 4 h gave a mixture of **2** and **3** in a ratio of *ca.* 1:1 as determined by NMR spectroscopy. Both compounds were isolated by fractional crystallization. The results of elemental analysis of **3** correspond to the formula $C_{13}H_{13}NO_6$, confirmed by the appearance of the molecular ion peak at *m/e* 279, and its IR spectrum shows the presence of a carbonyl (1715) and nitro olefin (1660 and 1515 cm^{-1}) group but the absence of a hydroxyl and an *O*-acetyl group. The NMR spectrum revealed that the product had lost the glycosidic methoxyl group but retained the benzylidene group. One proton singlet at δ 8.08 was assigned to the formyl proton, its chemical shift agreeing with that of (4*S*,5*R*)-4-nitromethyl-2-phenyl-1,3-dioxan-5-yl formate (**5**).[2] The signals of olefinic protons (H-1 and H-2) overlapped to give a singlet at δ 7.24 with two proton intensity. In order to confirm the structure, the nitro olefin **3** was treated with hydrazoic acid to give the adduct **4**, the IR spectrum of which showed the presence of azide (2170), formyl (1725), and nitro (1560 cm^{-1}) groups, and NMR spectrum exhibited a singlet at δ 8.06 (–OCHO) but no signal at δ 7.24 region due to olefinic protons. Although all the signals expected for **4** were observed and their assignments were verified by double-resonance experiments, the configuration at C-2 position has not been determined.

When acetylation was carried out at 0 °C and stopped after 20 min, the acetate **2** was formed almost exclusively. From this result and the fact[3] that hydration or the addition of acetic acid occurs readily to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside in aqueous pyridine or in pyridine–acetic acid solution the following route seems to be reasonable. Under the reaction conditions, elimination of methnol followed by the addition of acetic acid should give rise to the diacetate **6**,[4] which would be converted into the unstable nitro alcohol **7** during the course of isolation process. The C_1–C_2 bond cleavage of **7** facilitated by the nitro group[2] and the subsequent elimination of acetic acid should afford the nitro olefin **3**.



Experimental

Melting points were determined in capillaries and are uncorrected. IR spectra were recorded for KBr discs and NMR spectra for solutions in $CDCl_3$ (tetramethylsilane as internal standard) with a JNM-4H-100 (JEOL). Commercial acetic anhydride and pyridine were used without purification.

Acetylation of Methyl 4,6-O-Benzylidene-2-deoxy-2-nitro-β-D-glucopyranoside (1) with Acetic Anhydride–Pyridine. To a solution of the nitro alcohol **1** (1.02 g) in pyridine (8 ml) was added acetic anhydride (4 ml) at room temperature. The mixture was kept for 4 h and poured into 100 ml of ice water. The precipitate was filtered and washed thoroughly with water to give 964 mg of a crude product. The IR and NMR spectra indicated it to be a mixture of **2** and **3** (approximately 1:1). The crude product was recrystallized from ethyl acetate; the first crop was colorless crystals of **3** (410 mg): Mp 137.0—137.5 °C; $[\alpha]_D^{20}$ 0° (*c* 1, $CHCl_3$); IR 1715 (CO), 1660 and 1515 cm^{-1} (C=C–NO_2); NMR δ=8.08 (s, 1, CHO), 7.24 (s, 2, H-1 and H-2), 5.60 (s, 1, PhCH), 4.93 (sex, 1, H-4, $J_{3,4}$=10.0, $J_{4,5e}$=5.6, $J_{4,5a}$=10.0 Hz), 4.58 (d, 1, H-3), 4.51 (q, 1, H-5e, $J_{5a,5e}$=10.0 Hz), 3.71 (t, 1, H-5a), and 7.42 (broad s, 5, Ph).

Found: C, 56.11; H, 4.65; N, 4.92%. Calcd for $C_{13}H_{13}NO_6$: C, 55.91; H, 4.70; N, 5.02%.

The second crop (430 mg) was **2** containing small amounts of **3** as judged by its IR spectrum. Recrystallization from ethyl acetate gave pure **2** (380 mg), identical with an authentic sample.[1]

Addition of Hydrazoic Acid to the Nitro Olefin 3. To a solution of **3** (45 mg) in THF (3 ml) was added a chloroform solution containing hydrazoic acid (*ca.* 1.6 N, 0.15 ml). The mixture was stirred for 3 h at room temperature and then

evaporated *in vacuo* to give a crystalline residue (52 mg). The NMR spectrum showed the presence of two products in a ratio of approximately 5: 1. The major product crystallized from ethanol was 34.8 mg of **4**: Mp 137.5—138.0 °C; $[\alpha]_D^{20}$ +0.31° (*c* 0.6, $CHCl_3$); IR 2170 (N_3), 1725 (CHO), and 1560 cm^{-1} (NO_2); NMR δ=8.06 (s, 1, CHO), 7.38 (broad s, 5, Ph), 5.48 (s, 1, PhCH), 5.28 (sex, 1, H-4, $J_{3,4}$=9.7, $J_{4,5e}$=5.0, $J_{4,5a}$=10.0 Hz), 4.66 (d, 1, H-1, $J_{1,2}$=8.8 Hz), 4.65 (d, 1, H-1′, $J_{1',2}$=5.0 Hz), 4.51 (q, 1, H-5e, $J_{5e,5a}$=11.3 Hz), 4.21 (oct, 1, H-2, $J_{2,3}$=2.2 Hz), 4.01 (q, 1, H-3), and 3.68 (t, 1, H-5a).

Found: C, 48.62; H, 4.34; N, 17.51%. Calcd for $C_{13}H_{14}N_4O_6$: C, 48.45; H, 4.38; N, 17.39%.

References

1) T. Sakakibara and R. Sudoh, *Carbohydr. Res.*, **50**, 197 (1976).

2) T. Sakakibara, T. Takamoto, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **44**, 865 (1971).

3) T. Sakakibara and R. Sudoh, unpublished results.

4) Elimination of acetic acid appears to predominate that of methanol; the former should reversible but not the latter, resulting in the formation of the diacetate **6**.