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# REACTIONS OF β-D-HEXOPYRANOSIDE INVOLVING α-NITROOLEFIN STRUCTURE WITH SOME S-YLIDES

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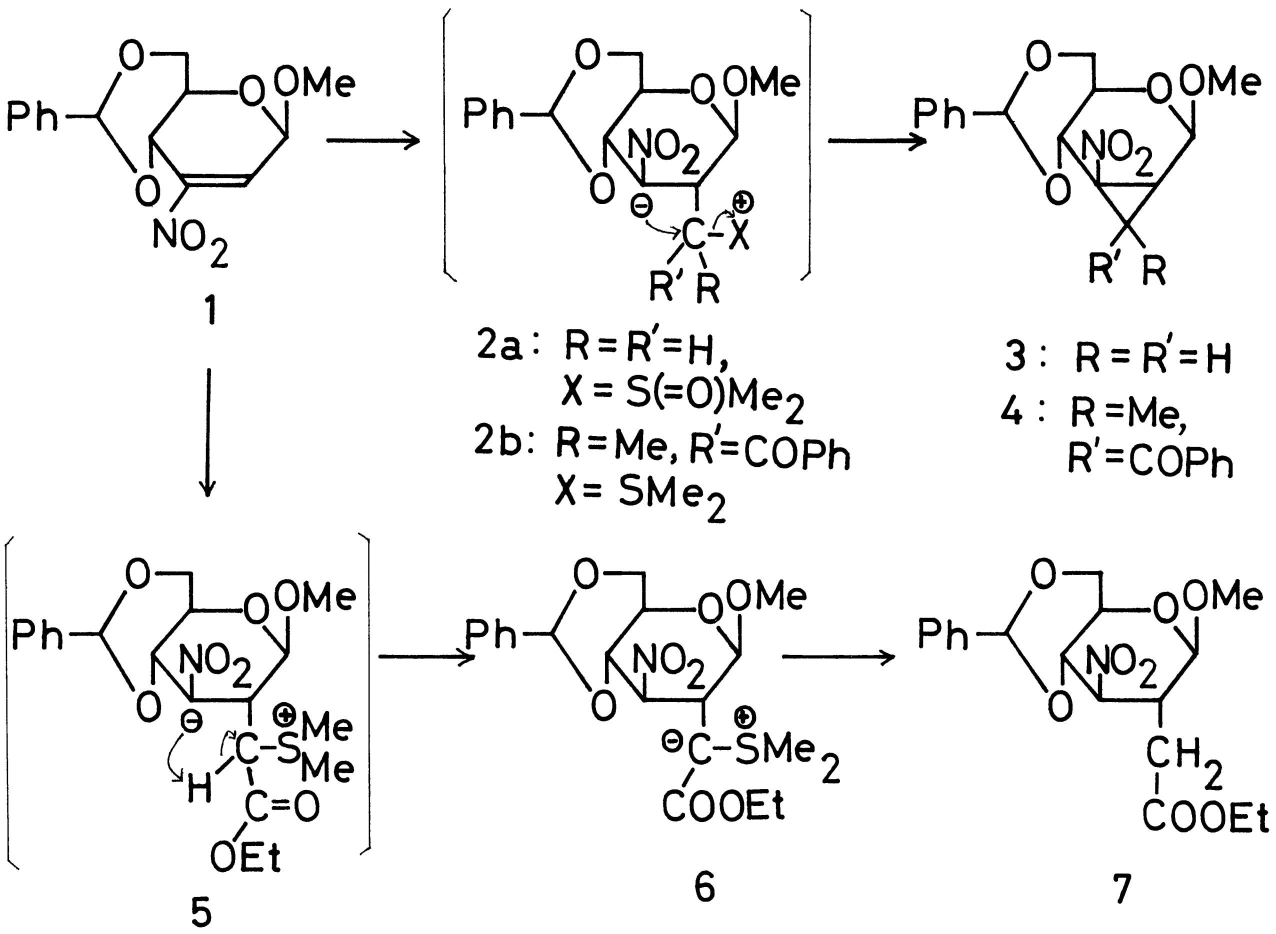
Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) with dimethylsulfoxonium methylide and dimethylsulfuranylidene acetophenone afforded the corresponding cyclopropane derivative **3** (75%) and **4** (71%), respectively. In the case of ethyl (dimethylsulfuranylidene) acetate, however, stable ylide (**6**) which involves two isomers was obtained in 75% yield. Catalytic reduction of **6** gave quantitatively ethoxycarbonylmethyl derivative (**7**) which has *gluco*-configuration.

In the field of carbohydrate chemistry, it has been known[1,2] that α- or β-D-pyranosides involving α-nitroolefin structure are easily converted to the corresponding α-nitroepoxides, and also both 2,3-anhydro-β-D-allo- and α-D-mannopyranoside bearing a nitro group at C-3 position exibit $J_{1,2}$=0 Hz in the p.m.r. spectra. While, there is only one report[3] which described the synthesis of α-nitrocyclopropanes from aliphatic α-nitroolefins with S-ylide. In this paper, we wish to present the synthesis of 3-nitro-β-D-hexopyranosides involving a cyclopropane ring which may be analogous to the epoxide sugars, and the isolation of a nitro sugar having a ylide moiety.

Reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) with dimethylsulfoxonium methylide[3] in dimethyl sulfoxide at room temperature for 1 hr afforded methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-(2R;3R)-methylene-3-nitro-β-D-*erythro*-hexopyranoside (**3**) {mp 147.5-148.0°C and $[\alpha]_D^{20}$ -44.2° (c 1, $CHCl_3$)} in 75% yield.

Assignment of the above configuration to **3** was based on $J_{1,2}$ value (0 Hz). This



Scheme 1

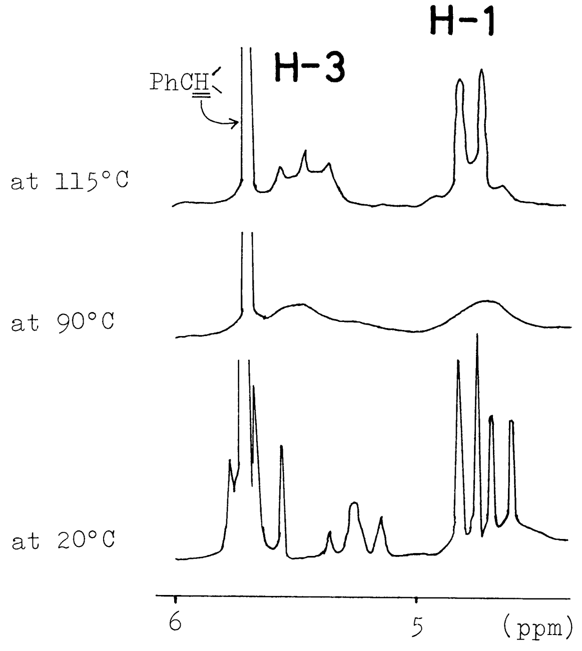


Fig. 1. Change of H-1 and H-3 signal in p.m.r. spectrum of 6 under elevated temperature (in DMSO-$d_6$).

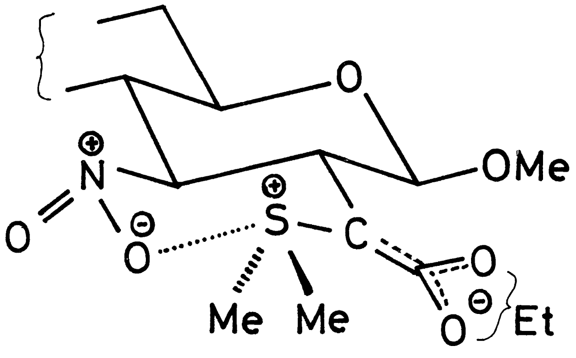


Fig. 2. Possible structures of the ylide moiety in 6.

value should also mean that a conformation of the product is similar to methyl 2,3-anhydro-4,6-*O*-benzylidene-3-nitro-β-D-allopyranoside.[1,2]

However, when **1** was treated with ethyl (dimethylsulfuranylidene) acetate[4] in tetrahydrofuran at room temperature for 18 hr followed by recrystallization from ethanol, a rare and stable compound,[5] i.e., methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-(dimethylsulfuranylidene ethoxycarbonylmethyl)-3-nitro-β-D-glucopyranoside (**6**) {mp 165.5-166.0°C and $[\alpha]_D^{20}$ +39° (c 1, $CHCl_3$)}, was obtained in 75% yield. The structure was determined by the following data: i) elemental analysis: molecular formula $C_{20}H_{27}NO_8S$; ii) i.r. (KBr): a specific absorption band of estercarbonyl group ($\nu$c=o) of ylide compounds at 1615 $cm^{-1}$, and $\nu_{as}NO_2$ at 1560 $cm^{-1}$; iii) MS: $M^+$ and $(M-OC_2H_5)^+$ peak at m/e 441 and 396,[6] respectively; iv) catalytic reduction on Pd-C,[7] accompanied with odor of dimethyl sulfide, gave quantitatively methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-(ethoxycarbonylmethyl)-3-nitro-β-D-glucopyranoside (**7**) {mp 146.0-146.5°C and $[\alpha]_D^{20}$ -47° (c 1, $CHCl_3$)} which has large coupling constants ($J_{1,2}$=7.5, $J_{2,3}$=10, and $J_{3,4}$=10 Hz).

P.m.r. spectrum (in DMSO-$d_6$) of **6** (Fig. 1) revealed that two stereoisomers, which may be geometrical isomers[8] as shown in Fig. 2, are existed in a ratio of ca. 1:1,[9] i.e., two doublets (at δ4.79 and 4.65) and two triplets (at δ5.66 and 5.25) corresponding to H-1 and H-3 signals appeared, respectively. With respect to the sugar ring, they have obviously the same configuration (*gluco*-form) and conformation (rigid C1 form) because of the same values for their coupling constants ($J_{1,2}$=7.5, $J_{2,3}$=10, and $J_{3,4}$=10 Hz) and the quantitative formation of **7** from **6** on the catalytic reduction. The facts may be explained by an anisotropy of the estercarbonyl group which has two geometries (Fig. 2). Furthermore, it is reasonable to assume that the considerable stability factor is based on an interaction between an oxygen atom of the nitro group and the sulphur atom. The assumption was also supported by the p.m.r. studies under elevated temperature (20-115°C).

Finally, a similar reaction of **1** with dimethylsulfuranylidene acetophenone gave methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-(2R;3S)-(1-benzoylethylidene)-3-nitro-β-D-*erythro*-hexopyranoside (**4**)[10] {mp 143-144°C and $[\alpha]_D^{20}$ -68° (c 1, $CHCl_3$)} in 71% yield. The small value for coupling constant ($J_{1,2}$=1.3 Hz) of **4** indicates that the methoxy group and the cyclopropane ring are oriented in a *trans*-relationship.

These reactions may proceed as shown in Scheme 1, i.e., a hydrogen atom attaching the ylide moiety in the intermediate (**5**) is easily abstracted, compared with that in **2a**. Therefore, it migrates to the carboanion (C-3) to give ylide **6**, and the carboanion (C-3) in **2a** attacks ylide carbon to give **3**. But in **2b** which has no active hydrogen atom, such a migration doesn't occur.

Table 1. P.m.r. data at 100 MHz (TMS as an internal standard in $CDCl_3$)

| Compound | | **3** | **4** | **6** | **7** |
|---|---|---|---|---|---|
| Chemical Shift (ppm) | H-1 | 4.52 (s) | 5.77 (d) | 4.96 (d) 4.71 (d) | 4.65 (d) |
| | H-2 | 2.28 (t) | 2.57 (d) | 3.6～3.5 (m) | 2.7～2.5 (m) |
| | H-3 | - | - | 5.84 (t) 5.40 (t) | 5.02 (t) |
| | H-4 | 4.96 (d) | 4.64 (d) | 4.09 (t) | 4.15 (t) |
| | H-5 | 2.99 (six) | 3.15 (six) | 4.06 (six) | 3.52 (six) |
| | $H-6^a$ | 3.75 (t) | 3.57 (t) | 3.74 (t) | 3.82 (t) |
| | $H-6^e$ | 4.23 (q) | 4.12 (q) | 4.40 (q) | 4.37 (q) |
| | $H_{exo}$* | 2.28 (t)** | - | - | - |
| | $H_{endo}$* | 1.64 (t) | - | - | - |
| Coupling Constant (Hz) | $J_{1,2}$ | 0 | 1.3 | 7.5 | 7.5 |
| | $J_{2,3}$ | - | - | 10 | 10 |
| | $J_{3,4}$ | - | - | 10 | 10 |
| | $J_{4,5}$ | 10 | 10 | 10 | 10 |
| | $J_{5,6a}$ | 10 | 10 | 10 | 10 |
| | $J_{5,6e}$ | 5 | 5 | 5 | 5 |
| | $J_{6a,6e}$ | 10 | 10 | 10 | 10 |
| | $J_{ex,en}$ | 6 | - | - | - |
| | $J_{2,ex}$ | 6 | - | - | - |
| | $J_{2,en}$ | 6 | - | - | - |

* Proton of the cyclopropane ring.

** This signal has a slight long-range coupling with the H-4.

## References and Notes

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5). This compound was isolated as yellow fine crystals. Sugar involving a ylide structure is otherwisely unknown. When heated under reflux in benzene, this ylide was quantitatively recovered although this type of ylides is generally unstable.

6). Appearance of $M^+$ peak indicates that ylide **6** is very stable.

7). In this step, the nitro group was not reduced because dimethyl sulfide may weaken the ability of the catalyst.

8). Possibility of rotational isomers with respect to the bond of C-2 and ylide carbon can not be completely discarded.

9). In the case of $CDCl_3$ the spectrum also showed the ratio of 1:1.

10). The configuration of the other chiral carbon in the cyclopropane ring was not determined, but the benzoyl group may be oriented in exo by virtue of steric hindrance.

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