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A FACILE PREPARATION OF α-NITROOLEFIN OF CARBOHYDRATES

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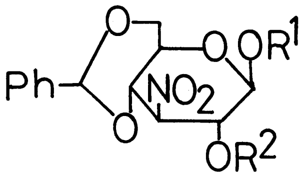
D-Hexopyranosides involving β-nitro alcohol were readily converted to the corresponding α-nitroolefins via sulfonates when mainly treated with ca. 1 eq. mesyl chloride-ca. 2 eq. triethylamine in CH_2Cl_2 or THF, whereas methyl 3-deoxy-2-*O*-methylsulfonyl-3-nitro-*α*-*D*-glucopyranoside derivative **10** was isolated in 80% yield when 1 eq. Et_3N was used.

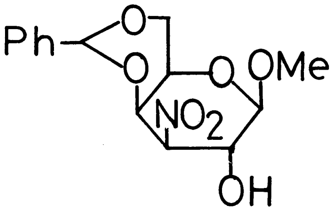
In the field of carbohydrate chemistry, it is well known that α-nitroolefins are extremely reactive and are useful intermediates for the syntheses of polyamino,[1] branched-chain sugars,[2] etc.[3,4] Particularly, it is noteworthy that addition reactions of weak acids such as hydrazoic acid and hydrogen cyanide without catalyst,[5] and of active methylene compounds with phase-transfer catalyst[6] to several pyranosides involving α-nitroolefin give the corresponding thermodynamically less stable products selectively. On the other hand, pyranosides involving α-nitroolefin are generally prepared from the corresponding acetates by Schmidt-Rutz reaction[7] which takes a long time[8] under reflux condition. Therefore a shorter and milder procedure than above one is necessarily required.

Methylsulfonoxy function[9] is a favorable leaving group on such an elimination reaction because of better elimination activity than that of acetoxy group and of no affecting the reaction system after elimination. Methyl 4,6-*O*-benzylidene-3-deoxy-3-nitro-*β*-*D*-glucopyranoside[10] (**1**) was treated[11] with 1.1 eq. methanesulfonyl chloride (MsCl) in the presence of 2.1 eq. of triethylamine (Et_3N) in methylene chloride (CH_2Cl_2) at r.t. for 5 min to give the nitroolefin[10] (**2**) in 84% yield. In this reaction, however, **2** and its precursor **3** were obtained together with **1** when 1.0 eq. of Et_3N was used. Similarly, phenyl glucoside[12] (**4**) underwent sulfonylation-elimination reaction in tetrahydrofuran (THF) or CH_2Cl_2 to afford the nitroolefin[12] (**5**) in 94% yield. In the case of methyl galactopyranoside[13] (**6**), 4.1 eq. Et_3N-2.3 eq. MsCl in THF was used to give the nitroolefin[13] (**7**) in 96% yield although the reaction was incomplete in 2.3 eq. Et_3N-1.2 eq. MsCl system.

In *α*-*D*-glucoside series, on the other hand, the sulfonate (**10**) was isolated as stable product. Treatment of methyl α-D-glucoside[13] (**8**) with 1.0 eq. Et_3N-1.1 eq. MsCl in CH_2Cl_2 gave methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methylsulfonyl-3-nitro-*α*-*D*-glucopyranoside **10**; mp 219.5-220.5° and $[\alpha]_D^{23}$ +9.0° (c 1, acetone), in 80% yield which was readily converted to the nitroolefin[14] (**9**) by Et_3N. **9** was also obtained directly from **8** with 2.1 eq. Et_3N-1.1 eq. MsCl system in 89% yield.



1: R^1=Me, R^2=H
3: R^1=Me, R^2=SO$_2$Me
4: R^1=Ph, R^2=H



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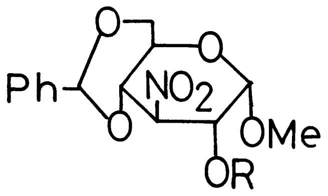
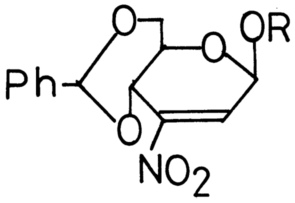
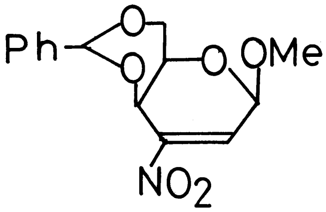


8: R=H
10: R=SO$_2$Me



2: R=Me
5: R=Ph



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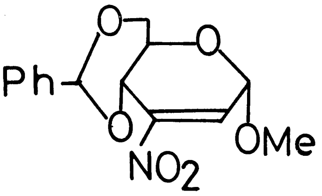

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