Tetrahedron Letters, Vol. 34, No. 21, pp. 3433-3434, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

First Preparation of Pyranosid Nitroolefin Having a Peroxy Group and Its Reaction with Some Nucleophiles

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Summary: Treatment of nitroalkene 1 with t-butyl hydroperoxide and m-chloroperbenzoic acid gave the SN2' product and 2,3-anhydro derivative, respectively, in high yields. The former product is proved to be useful intermediate for introduction of nucleophiles at C-4.

To our best knowledge, there is no report for preparation of nitro sugars having a reactive peroxy group. In general the reactions of nitroalkenes with peroxide such as *t*-butyl hydroperoxide give the nitro epoxide for its facile cleavage of the O-O bond.[1] Assuming that the reaction between a hydroperoxide and nitroalkene having a good leaving group at the β'-position affords the SN2' product, we have performed the reaction of **1** with *t*-butyl hydroperoxide and indeed obtained the intending peroxy product **4** in high yield.

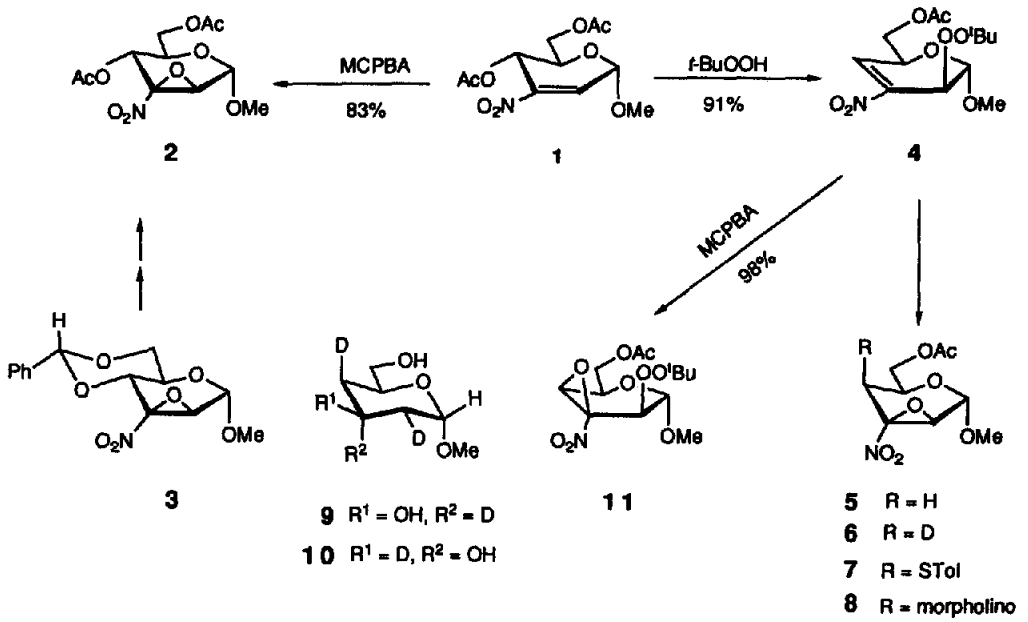
Reaction of **1** with *m*-chloroperbenzoic acid (MCPBA) in the presence of 1.1 equimolar amount of 1M NaOH afforded the nitroepoxide **2** [2] in 83% yield. The *manno* configuration of **2** is suggested by $J_{1,2}$ value (0 Hz)[3] and confirmed by its identification with an authentic sample prepared by debenzylidenation and subsequent acetylation of 4,6-*O*-benzylidene derivative **3**.[3,4] When **1** was similarly treated with *t*-butyl hydroperoxide, the peroxide **4** was obtained in 91 % yield, after purification with short column chromatography. Thus isolated peroxide **4** [2] was unexpectedly stable and could be kept at least one week at 20° and its structure was determined by elemental analysis, IR, and ^{1}H-NMR spectroscopy.

Although introduction of nucleophiles at the C-2 position had been carried out extensively,[5] similar reactions at the C-4 position of 3-nitro sugars are rather scarce. Since the peroxide **4** has potential utility for introducing nucleophiles at C-4, **4** was subjected to the reaction with sodium borohydride to give the 4-deoxy derivative **5** [2] in 97% yield. The attack of a hydride ion from the upper side was proved by the use of sodium borodeuteride. On exposure to *p*-toluenethiol, **4** smoothly converted to the 4-mercapto derivative **7** [2] in 95 % yield. Morpholine similarly led to the 4-morpholino derivative **8** [2] in 82% yield. The *talo*-configurations of these products were determined on the basis of $J_{1,2}$ (ca. 0 Hz) and $J_{4,5}$ values (3.0 - 5.0 Hz), and confirmed chemically in the case of **6** by treatment with lithium aluminum deuteride. SN2-Cleavage of the oxirane ring gave the 3-ulose, which then reduced to the alcohols **9** and **10**.[4] Equatorial and axial protons of C-2 and C-4 were deuterated in these 3-epimeric products **9** and **10**.

The peroxydation not only gave synthetically useful intermediate **4** as mentioned above, but also afforded a useful information about the reaction mechanism. It is not established whether the SN2' reaction of α-nitroalkene with a leaving group at the β'-position proceeds in a concerted mechanism or stepwise, i.e. via a nitronate ion.[6] The peroxide **4** is the SN2' product, but the nitro epoxide **2** is not. It is most likely that a nucleophile adds the C-2 position, giving a nitronate ion, the anion of which attacks the perbenzoyl group for its facile cleavage of the O-O bond, while it expels the acetoxyl group at C-4 as a leaving group instead of a

relatively strong O-O bond of *t*-butylperoxide moiety. Thus it may conclude that the SN2' product **4** also generated by the stepwise mechanism rather than concerted one.

As expected from the stepwise mechanism, treatment of **4** with MCPBA afforded the 3,4-anhydro derivative **11** [2] in 98 % yield.



References and Notes

1. For example, T. Sakakibara, T. Minami, Y. Ishido, and R. Sudoh, Carbohydr. Res., **1982**, 109, 167-179.
2. All new compounds gave satisfactory elemental analyses. Physical data and part of ^{1}H-NMR data are as follows. Compound **2**, syrup, $[\alpha]_D$ +66.6° (*c* 1.1, $CHCl_3$); IR 1750 (OAc) and 1560 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ=4.97 (s, 1H, H-1), 3.89 (broad s, 1H, $J_{2,4}$=1.0 Hz, H-2), and 5.51 (dd, 1H, $J_{4,5}$=8.9 Hz, H-4). **4**, syrup, $[\alpha]_D$ +7.1° (*c* 1.2, $CHCl_3$); IR 1745 (OAc) and 1535 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ=5.30 (d, 1H, $J_{1,2}$=1.0 Hz, H-1), 4.97 (dd, 1H, $J_{2,5}$=2.0 Hz, H-2), 7.45 (d, 1H, $J_{4,5}$ 2.0 Hz, H-4). **5**, 57-57.5°C, $[\alpha]_D$ +100.3° (*c* 1.2, $CHCl_3$); IR 1730 (OAc) and 1560 cm^{-1} (NO_2); ^{1}H-NMR (C_6D_6) δ=4.27 (s, 1H, H-1), 3.23 (s, 1H, H-2), 1.58 (dd, 1H, $J_{4a,4e}$=14.9, $J_{4a,5}$=11.6 Hz, H-4a), 2.51 (dd, 1H, $J_{4e,5}$=4.3 Hz, H-4e). **7**, 157.5-158.5°C, $[\alpha]_D$ +90.8° (*c* 0.8, $CHCl_3$); IR 1740 (OAc) and 1560 cm^{-1} (NO_2); ^{1}H-NMR (C_6D_6) δ=4.28 (s, 1H, H-1), 3.30 (s, 1H, H-2), 4.76 (d, 1H, $J_{4,5}$=3.6 Hz, H-4). **8**, 68.5-69.5°C, $[\alpha]_D$ +101.8° (*c* 0.8, CH_2Cl_2); IR 1740 (OAc) and 1570 cm^{-1} (NO_2); ^{1}H-NMR (C_6D_6) δ=4.24 (s, 1H, H-1), 2.94 (s, 1H, H-2), 4.10 (d, 1H, $J_{4,5}$=5.0 Hz, H-4). **11**, syrup, $[\alpha]_D$ +36.1° (*c* 0.9, CH_2Cl_2); IR 1750 (OAc) and 1570 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ=4.73 (s, 1H, H-1), 5.42 (s, 1H, H-2), 3.79 (s, 1H, $J_{4,5}$=0 Hz, H-4).
3. H. H. Baer and W. Rank, Can. J. Chem., **1971**, 49, 3192-3196.
4. T. Nakagawa and T. Sakakibara, Carbohydr. Res., **1987**, 163, 227-237.
5. For example, T. Sakakibara, N. Ohkita, and T. Nakagawa, Bull. Chem. Soc. Jpn., **1992**, 65, 446-451.
6. D. Seebach and P. Knochel, Helv. Chim. Acta, **1984**, 67, 261-283.

(Received in Japan 21 December 1992)