Carbohydrate Research, 160 (1987) c3–c5
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

Preliminary communication

Preparation and nucleophilic addition reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*erythro*-hex-2-enopyranoside; synthetic utility of α-sulfonylalkene intermediates in carbohydrate chemistry

TOHRU SAKAKIBARA*,

Department of Chemistry, Yokohama City University, Seto, Kanazawa-ku, Yokohama 236 (Japan)

IZUMI TAKAI, YOSHIFUSA TACHIMORI, AZUMA YAMAMOTO, YOSHIHARU ISHIDO*, AND (the late) ROKURO SUDOH

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

(Received October 10th, 1986, accepted for publication, November 25th, 1986)

α-Sulfonylalkenes have potential utility for organic synthesis, because, for example, the sulfonyl group, after introduction of a nucleophile at its β-position, can be used as a means of introducing a carbonyl group[1] or a double bond[2], or be replaced by a hydrogen atom[3]. Despite such versatility, no studies of a sugar derivative having an α-sulfonylalkene moiety on a pyranose ring have been reported. Pyranose derivatives having a 2-phenylsulfonyl-2-trimethylsilylvinyl group at position 5 have been used as intermediates for the synthesis of maytansinoids[4].

We now report the synthesis of some 2-*C*-*p*-tolylsulfonyl-2-enopyranosides, and the reaction of the title compound with several nucleophiles, including desulfonylation *via* the epoxide derivative **15**.

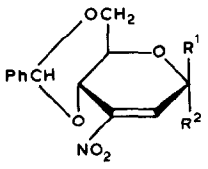
As already reported[5], toluene-*p*-sulfinic acid reacts with methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-*p*-tolylsulfonyl-β-D-glucopyranoside (**3**) in high yield. Treatment of **3** with triethylamine at room temperature afforded 90% of the desired methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*erythro*-hex-2-enopyranoside (**4**) {m.p. 149–150°, $[\alpha]_D^{25}$ −81° (*c* 1.5, chloroform)}**. Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-β-D-*threo*-hex-2-enopyranoside (**6**) provided methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-*p*-tolylsulfonyl-β-D-galactopyranoside (**8**) {91%, m.p. 239° (dec.), $[\alpha]_D^{25}$ +17° (*c* 1, acetone); $J_{1,2}$ 8.6, $J_{2,3}$ 12, and $J_{3,4}$ 4.5 Hz}. Elimination of nitrous acid from **8** with triethylamine gave 65% of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-*threo*-

*To whom correspondence should be addressed.

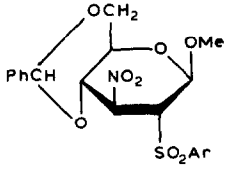
**Satisfactory elemental analyses were obtained for all new compounds.

0008-6215/87/$ 03 50

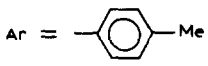
hex-2-enopyranoside (**7**) {m.p. 154.5–155°, $[\alpha]_D^{25}$ −185° (*c* 0.6, chloroform)}. Similar reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-α-D-*erythro*-hex-2-enopyranoside (**2**) gave methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-2-*C*-*p*-tolylsulfonyl-α-D-mannopyranoside (**9**) {86%, m.p. 175–176°, $[\alpha]_D^{25}$ ~0° (*c* 1, chloroform); $J_{1,2}$ 0.7, $J_{2,3}$ 5.3, and $J_{3,4}$ 11 Hz}, which was similarly converted into ~55% of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-α-D-*erythro*-hex-2-enopyranoside (**5**) {m.p. 133–134°, $[\alpha]_D^{25}$ +226° (*c* 1, chloroform)}; the yield depended on the conditions of the reaction.

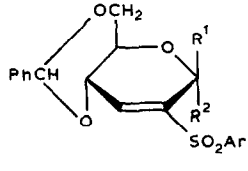


1 R^1 = OMe, R^2 = H
2 R^1 = H, R^2 = OMe

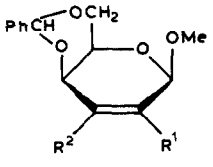


3

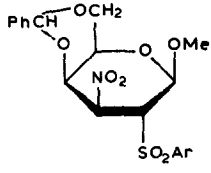




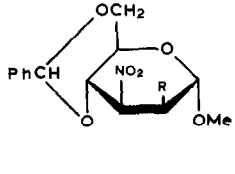
4 R^1 = OMe, R^2 = H
5 R^1 = H, R^2 = OMe



6 R^1 = H, R^2 = NO_2
7 R^1 = SO_2Ar, R^2 = H



8



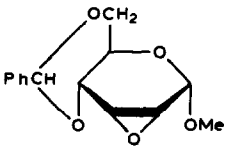
9 R = SO_2Ar

Compound **5** was also prepared by treatment[6] of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**10**) with sodium *p*-methylthiophenoxide to give methyl 4,6-*O*-benzylidene-2-thio-2-*S*-*p*-tolyl-α-D-altropyranoside (**11**, not isolated), oxidation of which with *m*-chloroperoxybenzoic acid, followed by *O*-mesylation and then elimination of methanesulfonic acid, gave **5** (47% from **10**).

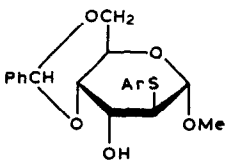
Sulfonylalkenes thus prepared should be reactive toward nucleophiles. The β-anomer **4** reacted with methanol, in the presence of a catalytic amount of sodium methoxide, to give 82% of methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-2-*C*-*p*-tolylsulfonyl-β-D-glucopyranoside (**12**) {m.p. 130–130.5°, $[\alpha]_D^{25}$ −80° (*c* 0.87, chloroform); $J_{1,2}$ 7.5, $J_{2,3} = J_{3,4}$ = 9.0 Hz}. Reaction of **4** with aqueous ammonia in tetrahydrofuran, followed by acetylation, afforded a mixture of two products, from which 71% of methyl 3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-*p*-tolylsulfonyl-β-D-glucopyrnaoside (**13**) {m.p. 203–204°, $[\alpha]_D^{25}$ −61° (*c* 0.87, chloroform); $J_{1,2}$ 8.3, $J_{2,3} = J_{3,4}$ = 10 Hz} was isolated. Treatment of **4** in refluxing nitromethane containing triethylamine provided 78% of methyl 4,6-*O*-benzylidene-

2,3-dideoxy-3-*C*-nitromethyl-2-*C*-*p*-tolylsulfonyl-β-D-glucopyranoside (**14**) {m.p. 185.5–186°, $[\alpha]_D^{25}$ −54° (*c* 1, chloroform); $J_{1,2}$ 7.1, $J_{2,3} = J_{3,4} = 10.5$ Hz}. Treatment of **4** with hydrogen peroxide in the presence of sodium hydroxide gave 93% of methyl 2,3-anhydro-4,6-*O*-benzylidene-2-*C*-*p*-tolylsulfonyl-β-D-mannopyranoside (**15**) {m.p. 146–147°, $[\alpha]_D^{25}$ −80° (*c* 0.67, chloroform)}. The β-D-*manno* configuration of **15** was determined unequivocally by desulfonylation with lithium aluminium deuteride, leading to the alcohol[7] **16**. Desulfonylation also occurred on treatment of **15** with methylmagnesium iodide (2.4 equiv.), giving 70% of known[7] methyl 4,6-*O*-benzylidene-3-deoxy-β-D-*erythro*-hexopyranosid-2-ulose (**17**).

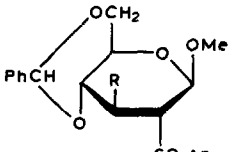
Thus, the α-sulfonylalkenes, readily prepared by two methods, have potential as synthetic intermediates in carbohydrate chemistry.



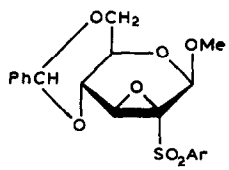
10



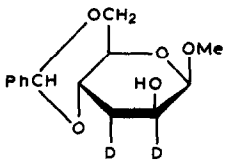
11



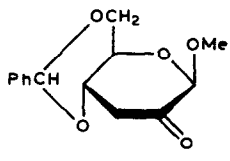
12 R = OMe
13 R = NHAc
14 R = CH_2NO_2



15



16



17

REFERENCES

1 R. D. Little and S O. Myong, *Tetrahedron Lett.*, (1980) 3339–3342
2 G Chirico, V Fiandanese, G Marchese, F. Naso, and O. Sciacovelli, *J. Chem. Soc., Chem Commun.*, (1981) 523–524
3 A. K Colter and R. E. Miller, Jr., *J. Org. Chem.*, 36 (1971) 1898–1903.
4 M Isobe, M. Kitamura, and T. Goto, *J. Am. Chem. Soc*, 104 (1982) 4997–4999; M Isobe, *Yuki Gosei Kagaku Kyokai Shi*, 41 (1983) 51–61.
5 T Sakakibara and R Sudoh, *J. Org. Chem*, 42 (1977) 1746–1750
6 S Hanessian and A. P A Staub, *Carbohydr Res.*, 16 (1971) 419–433
7 E H. Williams, W. A. Szarek, and J K N Jones, *Can J Chem.*, 49 (1971) 796–799.