Tetrahedron Vol. 44, No. 14, pp. 4569 to 4573, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00
Pergamon Press plc

THE HIGH-PRESSURE REACTION OF 2,5-DIMETHYLFURAN WITH 2,3-O-ISOPROPYLIDENE-D-GLYCERALDEHYDE[1]

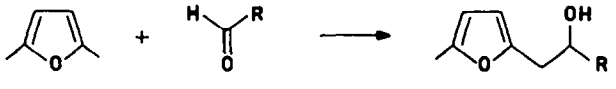
JANUSZ JURCZAK* AND STANISŁAW PIKUL

Institute of Organic Chemistry, Polish Academy of Sciences,
01-224 Warszawa, Poland

(*Received in UK* 23 *February* 1988)

Abstract - The asymmetric high-pressure reaction of 2,5-dimethylfuran (1) with 2,3-O-isopropylidene-D-glyceraldehyde (4) and chemical transformation of the resulting product 5 to 2-deoxy-D-pentitol derivatives (13, 14, and 15) are described.

Recently, we have described[2] a high-pressure reaction between 2,5-dimethylfuran (1) and activated compounds of type 2 (e.g. R=CO_2Et), which leads to products of general structure 3 corresponding to formal electrophilic substitution at the methyl group of the heteroaromatic system (Scheme 1). Likewise, 2,5-disubstituted thiophenes and pyrroles undergo a similar reaction.[3] In case of sterically hindered or non-activated carbonyl substrates, higher pressures and elevated temperatures are necessary to force the reaction to occur.[2,3]



1 2 3

Scheme 1

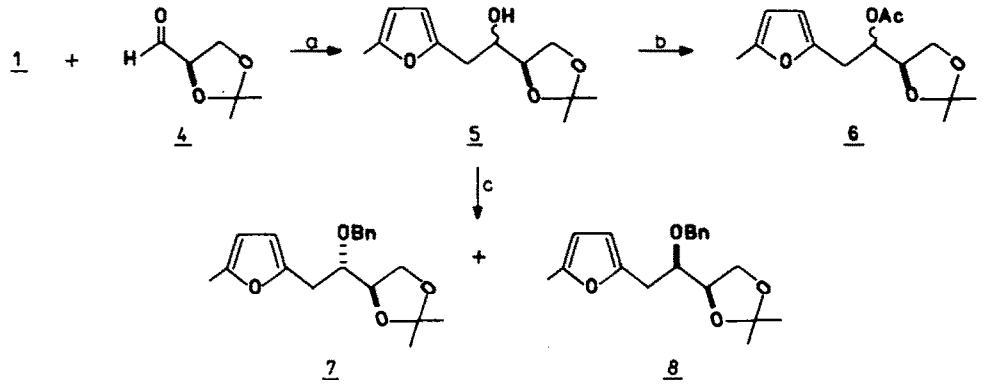
The products of the type 3 can constitute versatile synthons for the synthesis of carbohydrates and other polyhydroxylated natural products. This prompted us to study the course of asymmetric induction using 2,3-O-isopropylidene-D-glyceraldehyde (4)[4] as the chiral carbonyl substrate.

RESULTS AND DISCUSSION

When aldehyde 4 was subjected to the reaction with 1, carried out under 20 kbar pressure and at 55°C, compound 5 is formed as the sole, chromatographically pure product (Scheme 2). Since aldehyde 4 has only one chiral centre, the product 5 consists of two diastereoisomers in a ratio corresponding to the efficiency of the 1,2-induction process. This ratio was determined from the $Eu(fod)_3$-^{1}H NMR spectra of compounds 5 and 6 (cf. Experimental). In both cases the ratio was found to be 4:1.

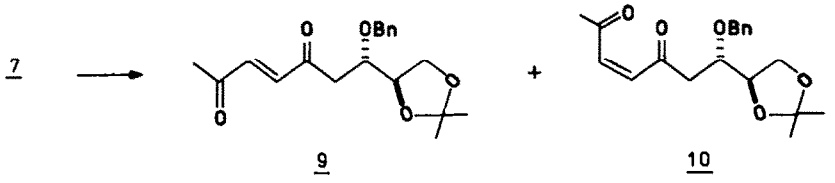
As shown in Scheme 2, the protection of the hydroxyl group of 5 with benzyl bromide afforded benzyl ethers 7 and 8, readily separable by column or thin-layer chromatography. This provided not only a further proof of diastereoselection in the high-pressure reaction, being fully consistent with ^{1}H NMR measurements, but also gives an access to optically pure compounds 7 and 8, which could serve as useful starting materials for further transformations. First, however, it was necessary to establish the absolute configuration of the newly created centre. For this purpose we used an

approach which could equally serve as a method for the synthesis of 2-deoxypentitols.



Scheme 2. Reagents and reaction conditions: (a) 20 kbar, 55°C, CH_2Cl_2; (b) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT; (c) BnBr, NaH, THF-DMF, RT.

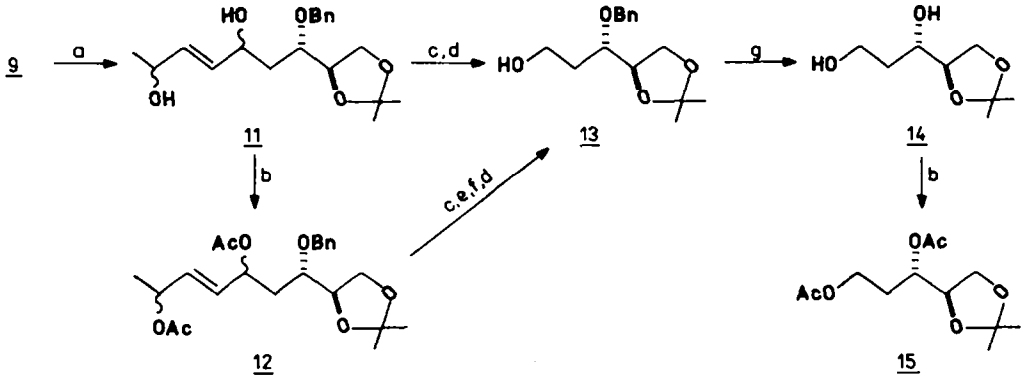
In the first step of chemical correlation, oxidative opening of the furan ring of the major diastereoisomer 7 was attempted. The treatment of 7 with pyridinium chlorochromate (PCC)[5] led to the desired product - *trans*-enedione 9 (Scheme 3). However, the reaction was very slow and stopped at a certain moment even though the substrate was still present in the reaction mixture, as evidenced by TLC. The inconvenience of the procedure prompted us to look for other solutions of the problem. Oxidative opening of the furan ring can also be effected using *meta*-chloroperbenzoic acid.[6] In this case, a mixture of geometrical isomers is usually obtained. When, however, the reaction of 7 with mCPBA was carried out at -10°C, pure *cis* compound (10) was obtained in 80% yield. Isomerization of *cis* compound (10) to the thermodynamically stable *trans* isomer (9) could be achived in 95% yield using iodine in hexane. Thus, a more convenient sequence, alternative to PCC oxidation, was established.



Scheme 3

In the meantime, a new method for oxidative opening of 2,5-disubstituted furan derivatives was developed at this laboratory.[7] It involves the use of bromine as oxidant which cleanly transforms 2,5-disubstituted furans to enediones when the reaction is carried out in an acetone-water mixture as solvent. This new procedure proved to be very useful also in case of 7. The reaction carried out in the presence of pyridine afforded - after flash chromatography - enedione *trans*-9 in 82% yield. Diisobutylaluminium hydride (DIBAL) reduction of 9, performed in a methylene chloride - hexane mixture at -78°C, led to diol 11 which was then acetylated to give diacetate 12 in 75% yield (Scheme 4). The crude diol 11 was transformed in two steps to 3-O-benzyl-4,5-O-isopropylidene-2-deoxypentitol 13. Osmium tetroxide - sodium periodate oxidation[8] of the double bond, carried out in aqueous dioxane at room temperature, gave an intermediate aldehyde which upon treatment with sodium borohydride in methanol afforded 13 in 35% overall yield. Alternatively, the transformation could be brought about starting from diacetate 12, through a four-step sequence of reactions. Osmium tetroxide - sodium periodate oxidation was performed similarly as in case of 11. The resulting α-acetoxy aldehyde was then subjected to lithium aliminium hydride reduction, carried out in ethyl ether, giving the respective *vic*-diol which was splitted by sodium periodate in aqueous me-

thanol. The product of this reaction was reduced with sodium borohydride, and after chromatographic purification it provided compound 13 in 45% overall yield. Thus, the latter sequence, even though by three steps longer, was found to give 2-deoxypentitol derivative 13 with a slightly higher yield as compared to the former one.



Scheme 4. Reagents and reaction conditions: (a) DIBAL, CH_2Cl_2 - hexane, -78°C; (b) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT; (c) OsO_4, $NaIO_4$, H_2O - dioxane, RT; (d) $NaBH_4$, MeOH, 0°C → RT; (e) $LiAlH_4$, Et_2O, 0°C → RT; (f) $NaIO_4$, H_2O - MeOH, RT; (g) H_2, Pd/C, MeOH, RT.

The route from 13 to the known compound 15 was straightforward: hydrogenolysis of 13, carried out in a Parr apparatus with palladium-on-charcoal as catalyst and methanol as solvent, afforded diol 14 which after acetylation (performed under standard conditions) gave 1,3-di-O-acetyl-4,5-O--isopropylidene-2-deoxypentitol 15 in 48% overall yield. Specific rotation of 15 was $[\alpha]_D$ -21.0° (c 0.66, chloroform), whereas identically protected 2-deoxy-D-ribitol and 2-deoxy-D-xylitol have been reported[9] to have specific rotations $[\alpha]_D$ -23.2°(c 0.63, chloroform) and $[\alpha]_D$ +36.7° (c 0.29, chloroform), respectively. This established unequivocally the absolute configuration at the newly created centre of chirality, shown in Schemes 2, 3, and 4.

The high-pressure reaction between 2,5-dimethylfuran (1) and 2,3-O-isopropylidene-D-glyceraldehyde (4) offers an access to optically pure synthons potentially applicable in the synthesis of natural products. High versatility of the furan ring as a precursor of open-chain systems has recently been proved by us[10] for other chiral furan derivatives obtained from aldehyde 4.

EXPERIMENTAL

The ^1H NMR spectra were recorded with a Jeol JNM-4H-100 (100 MHz) or a Varian EM-360 (60 MHz) spectrometer for $CDCl_3$ solutions (δ scale, TMS=0). The IR spectra were taken with a Beckman IR-4240 spectrophotometer. Optical rotations were measured with a Perkin-Elmer PE-141 spectropolarimeter.

Unless otherwise indicated, all reaction work-ups involved washing the organic layer with brine, drying over $MgSO_4$, and evaporation under reduced pressure. Preparative flash chromatography was performed on Merck Kieselgel 60 (239-400 mesh), according to Still's procedure.[11] All chromatographic separations were monitored by TLC and/or ^1H NMR. TLC was performed on Merck DC Alufolien Kieselgel 60 F-254. The reported yields refer to chromatographically pure compounds.

All high-pressure reactions were carried out in a piston-cylinder type apparatus with working volume of about 90 mL. Construction details have been reported previously.[12] The pressure inside the working volume was measured with a calibrated coil exact to ± 0.1 kbar. The accuracy of temperature measurements using a calibrated thermocouple was ± 1°C.

2,3-O-Isopropylidene-D-glyceraldehyde (4) was prepared from D-mannitol according to Kierstead's modification[13] of the known procedure.[14]

(2R,3ξ)-1,2-O-Isopropylidene-4-[2-(5-methylfuryl)]-1,2,3-butanetriol (5). A solution of 1 (706 μL, 6.6 mmol) and freshly prepared 4 (285 mg, 2.2 mmol) in CH_2Cl_2 (4 mL) was charged into a Teflon ampoule[15] placed in a high-pressure vessel filled with pentane as a transmission medium and compressed (20 kbar) at 50°C for 24 h. After cooling and decompression, the reaction mixture was concentrated to dryness and the residue was subjected to flash chromatography (ligroin - ethyl acetate 7:3) to give 110.1 mg (22% yield) of 5 as a colourless oil: $[\alpha]_D$ +35.0° (c 0.92, chloroform); IR (film), ν, 3300, 1565, 1250, 1140, 1040 cm^{-1}; ^1H NMR, δ, 6.09 (d, J = 2 Hz, 1 H), 5.97 (d, J = = 2 Hz, 1 H), 4.20-3.80 (m, 4 H), 2.95-2.77 (m, 3 H), 2.32 (s, 3 H), 1.49 (s, 3 H), 1.42 (s, 3 H). Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.80; H, 7.95. The ^1H NMR spectrum of 5 (25.9 mg) with $Eu(fod)_3$ (11.0 mg) showed the presence of two singlets corresponding to CH_3-furan at δ: 2.23 (0.6 H) and 2.36 (2.4 H).

(2R,3ξ)-3-O-Acetyl-1,2-O-isopropylidene-4-[2-(5-methylfuryl)]-1,2,3-butanetriol (6). To 249 mg (1.1 mmol) of 5 in CH_2Cl_2 (1.5 mL), 274 μL (2.0 mmol) of triethylamine, 156 μL (1.65 mmol) of acetic anhydride and a crystal of DMAP were added. After 3-h stirring at room temperature, the reaction mixture was diluted with Et_2O and worked up. The crude product was purified by flash chromatography (ligroin - ethyl acetate 3:1) to give 265.3 mg (90% yield) of 6 as a colourless oil: $[\alpha]_D$ +7.3° (c 1.72, chloroform); IR (film), ν, 1750, 1550, 1270, 1100, 1030 cm^{-1}; ^1H NMR, δ, 5.93 (bs, 2 H), 5.30-5.00 (m, 1 H), 4.30-3.70 (m, 3 H), 2.88 (d, J = 7 Hz, 2 H), 2.22 (s, 3 H), 2.03 (s, 3 H), 1.42 (s, 3 H), 1.33 (s, 3 H). Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.78; H, 7.64. The ^1H NMR spectrum of 6 (16.7 mg) with $Eu(fod)_3$ (16.0 mg) showed the presence of two singlets corresponding to CH_3-furan at δ: 2.33 (0.6 H) and 2.43 (2.4 H).

(2R,3S)- (7) and (2R,3R)-3-O-Benzyl-1,2-O-isopropylidene-4-[2-(5-methylfuryl)]-1,2,3-butanetriol (8). To a cold (0°C) suspension of sodium hydride (prepared from 320 mg of 50% NaH in mineral oil) in a mixture of 8 mL of THF and 2 mL of DMF, a solution of 1.31 g (5.8 mmol) of 5 in 2 mL of THF was added. The mixture was stirred for 0.5 h at room temperature, whereupon 0.8 mL (6.7 mmol) of benzyl bromide was added. After further 12 h of stirring, wet Et_2O was added and the mixture was worked up. The crude product was purified by column chromatography (ligroin - ethyl acetate 98:2) to give 1.32 g (72% yield) of 7 and 0.33 g (18% yield) of 8, both as colourless oils:
7: $[\alpha]_{578}$ -2.0° (c 1.61, chloroform); IR (film), ν, 1570, 1220, 1070 cm^{-1}; ^1H NMR, δ, 7.27 (m, 5 H), 5.95 (d, J = 3 Hz, 1 H), 5.83 (m, 1 H), 4.50 (s, 2 H), 4.10-3.60 (m, 4 H), 3.00-2.70 (m, 2 H), 2.25 (s, 3 H), 1.37 (s, 3 H), 1.29 (s, 3 H). Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.92; H, 7.78.
8: $[\alpha]_{578}$ +29.0° (c 1.18, chloroform); IR (film), ν, 1575, 1220, 1070 cm^{-1}; ^1H NMR, δ, 7.30 (m, 5 H), 5.96 (d, J = 3 Hz, 1 H), 5.83 (m, 1 H), 4.60 (s, 2 H), 4.30-3.60 (m, 4 H), 2.80 (d, J = 6 Hz, 2 H), 2.25 (s, 3 H), 1.43 (s, 3 H), 1.37 (s, 3 H). Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.17; H, 7.77.

E-(2R,3S)-3-O-Benzyl-1,2-O-isopropylidene-6-nonen-5,8-dione-1,2,3-triol (9). A. Compound 7 (316 mg, 1.0 mmol) and pyridine (322 μL, 4.0 mmol) were dissolved in 10 mL of an acetone - water mixture (85:15). The reaction mixture was vigorously stirred and cooled to -20°C, whereupon 54 μL (1.0 mmol) of bromine in 1.5 mL of precooled acetone - water (4:1) mixture was added. Subsequently the cooling bath was removed and the reaction mixture was stirred for 2 h at room temperature. Ethyl ether was then added and the mixture was worked up. The crude product was purified by flash chromatography (ligroin - ethyl acetate 4:1) to give 272.2 mg (82% yield) of 9 as a pale-yellow oil: IR (film), ν, 1690, 1625, 1260, 1075 cm^{-1}; ^1H NMR, δ, 7.37 (m, 5 H), 6.88 (s, 2 H), 4.63 (s, 2 H), 4.16-3.73 (m, 4 H), 3.00-2.80 (m, 2 H), 2.33 (s, 3 H), 1.38 (s, 3 H), 1.33 (s, 3 H). Calcd. for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.33; H, 7.39.
B. To 1.0 g (3.16 mmol) of 7 and 1.0 g (12.0 mmol) of sodium acetate in 70 mL of CH_2Cl_2, 4.0 g (18.6 mmol) of pyridinium chlorochromate were added. The reaction mixture was stirred for 10 h at room temperature and then refluxed for 9 h. After cooling, 50 mL of anhydrous Et_2O were added and the solution was filtered through Celite. The solvents were evaporated and the whole procedure was repeated two more times. The crude product was purified by flash chromatography (ligroin - ethyl acetate 4:1) to give 757.0 mg (75% yield) of compound 9.
C. To 166.0 mg (0.5 mmol) of compound 10 in 10 mL of hexane, some few crystals of iodine were added. The reaction mixture was stirred for 12 h at room temperature, whereupon 1 mL of 30% $Na_2S_2O_3$ aq was added and the mixture was worked up. After solvent evaporation, 158.0 mg (95% yield) of compound 9 were obtained.

Z-(2R,3S)-3-O-Benzyl-1,2-O-isopropylidene-6-nonen-5,8-dione-1,2,3-triol (10). To 189.6 mg (0.6 mmol) of 7 in 5 mL of CH_2Cl_2 cooled to -15°C, 114.0 mg (0.66 mmol) of m-chloroperbenzoic acid were added. The reaction mixture was kept for 36 h at -10°C, then washed with 5% NaOH aq and worked up. After drying (Na_2SO_4) and solvent evaporation at room temperature, the crude product was purified by flash chromatography (hexane - ethyl ether 3:1) to give 159.3 mg (80% yield) of 10 as a pale-yellow oil: IR (film), ν, 1700, 1610, 1210, 1070 cm^{-1}; ^1H NMR, δ, 7.39 (m, 5 H), 6.30 (s, 2 H), 4.63 (s, 2 H), 4.10-3.70 (m, 4 H), 2.85-2.70 (m, 2 H), 2.25 (s, 3 H), 1.34 (s, 3 H), 1.28 (s, 3 H).

E-(2R,3S,5ξ,8ξ)-3-O-Benzyl-1,2-O-isopropylidene-6-nonen-1,2,3,5,8-pentaol (11). To 283.5 mg (0.85 mmol) of 9 in 16 mL of a CH_2Cl_2 - hexane (1:1) mixture cooled to -78°C, 3.6 mL of a 1 M solution of DIBAL in hexane were added. The reaction mixture was stirred for 45 min, whereupon 3 mL of methanol were added, and the cooling bath was removed. At 0°C 0.5 mL of brine, 50 mL of ethyl ether and 5 g of anhydrous $MgSO_4$ were added, and the mixture was stirred for 1.5 h at room temperature. Filtration and evaporation of solvents gave 196.0 mg of crude 11 as a colourless oil which had to be immediately used for further reactions (compound 11 was analysed as its diacetate 12).

E-(2R,3S,5ξ,8ξ)-5,8-Di-O-acetyl-3-O-benzyl-1,2-O-isopropylidene-6-nonen-1,2,3,5,8-pentaol (12). To 273.6 mg (0.81 mmol) of crude 11 in 2 mL of CH_2Cl_2, 248 μL (1.82 mmol) of Et_3N, 159 μL (1.68 mmol) of Ac_2O and a crystal of DMAP were added. After 5-h stirring at room temperature, the reaction mixture was diluted with ethyl ether and worked up. The crude product was purified by flash chromatography (ligroin - ethyl acetate 95:5) to give 245.9 mg (75% yield calculated against 9) of

12 as a colourless oil: IR (film), ν, 1740, 1240, 1070 cm^{-1}; ^1H NMR, δ, 7.47 (m, 5 H), 5.83-5.35 (m, 4 H), 4.74 (AB system, J = 10 Hz, 2 H), 4.30-3.95 (m, 4 H), 2.08 (s, 6 H), 2.00-1.75 (m, 2 H), 1.50-1.20 (m, 12 H). Calcd. for $C_{23}H_{32}O_7$: C, 65.69; H, 7.76. Found: C, 65.68; H, 7.87.

3-O-Benzyl-4,5-O-isopropylidene-2-deoxy-D-ribitol (13). A. To 208.9 mg (0.62 mmol) of crude 11 in 5 mL of a dioxane - water (3:1) mixture, at room temperature 5.0 mg (0.02 mmol) of osmium tetroxide, followed - after 15 min - by 1.0 g (4.67 mmol) of sodium periodate, were added. The reaction mixture was stirred for 4 h; then 2 mL of 30% $NaHSO_3$ aq were added, followed by 20 mL of CH_2Cl_2. The residue obtained after work-up was dissolved in 4 mL of MeOH; the solution was cooled to 0°C and treated with 60.0 mg (1.8 mmol) of $NaBH_4$. The reaction mixture was stirred for 12 h at room temperature, diluted with Et_2O and worked up. The crude product was purified by flash chromatography (ligroin - acetone 5:3) to give 55.9 mg (35% yield calculated against 9) of 13 as a colourless oil: $[\alpha]_D$ +2.0° (c 3.65, chloroform); ^1H NMR, δ, 7.46 (m, 5 H), 4.75 (s, 2 H), 4.30-3.70 (m, 6 H), 1.86 (m, 2 H), 1.45 (s, 3 H), 1.38 (s, 3 H). Calcd. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.38; H, 8.40.

B. To 192.0 mg (0.46 mmol) of 10 in 3 mL of a dioxane - water (3:1) mixture, at room temperature 5.0 mg (0.02 mmol) of osmium tetroxide, followed - after 15 min - by 148.0 mg (0.69 mmol) of sodium periodate, were added. The reaction mixture was stirred for 3 h and worked up as in variant A. The crude product was dissolved in 20 mL of Et_2O, cooled to 0°C, and 90.0 mg (2.37 mmol) of $LiAlH_4$ were added. After 1-h stirring at room temperature, 90 μL of 15% KOH aq, and 270 μL of water were added, whereupon the mixture was filtered through Celite. The crude product obtained after evaporation of solvent was dissolved in 2 mL of MeOH, and treated with a solution of 200.0 mg (0.94 mmol) of sodium periodate in 3 mL of water. The reaction mixture was stirred for 1 h at room temperature, diluted with CH_2Cl_2 and worked up. The residue was subjected to $NaBH_4$ reduction, as described in variant A, and the crude product was purified by flash chromatography to give 67.3 mg (55% yield calculated against 10) of 13.

4,5-O-Isopropylidene-2-deoxy-D-ribitol (14). To 40.0 mg (0.15 mmol) of 13 in 10 mL of MeOH, a catalytic amount of palladium-on-charcoal was added, and the reaction mixture was shaken in a Parr apparatus for 7 h at room temperature under 3-atm hydrogen pressure. Filtration of catalyst and solvent evaporation, followed by flash chromatography (ligroin - acetone 1:1) afforded 17.0 mg (64% yield) of 14 as a colourless oil with specific rotation $[\alpha]_D$ +15.0° (c 0.67, chloroform).

1,3-Di-O-acetyl-4,5-O-isopropylidene-2-deoxy-D-ribitol (15). To 10.0 mg (0.057 mmol) of 14 in 0.5 mL of CH_2Cl_2, 16.4 μL (0.13 mmol) of Et_3N, 11.3 μL (0.12 mmol) of Ac_2O, and a crystal of DMAP were added. The reaction mixture was stirred for 4 h at room temperature, diluted with Et_2O and worked up. The crude product was purified by flash chromatography (ligroin - ethyl acetate 7:3) to give 11.0 mg (75% yield) of 15 as a colourless oil: $[\alpha]_D$ -21.0° (c 0.65, chloroform); ^1H NMR, δ, 5.10 (m, 1 H), 4.30-3.70 (m, 5 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 1.95 (m, 2 H), 1.42 (s, 3 H), 1.35 (s, 3 H).

Acknowledgment. Financial support from the Polish Academy of Sciences (Grant CPBP 01-13) is gratefully acknowledged.

REFERENCES

1. Preliminary communication: J. Jurczak and S. Pikul, *Tetrahedron Lett.*, 25, 3107 (1984).
2. J. Jurczak, T. Koźluk, S. Pikul, and P. Salański, *J. Chem. Soc., Chem. Commun.*, 1447 (1983).
3. G. Jenner, M. Papadopoulos, J. Jurczak, and T. Koźluk, *Tetrahedron Lett.*, 25, 5747 (1984).
4. J. Jurczak, S. Pikul, and T. Bauer, *Tetrahedron*, 42, 447 (1986).
5. G. Piancatelli, A. Scettri, and M. D'Auria, *Tetrahedron*, 36, 661 (1980).
6. R. D. Williams and E. LeGoff, *J. Org. Chem.*, 46, 4143 (1981).
7. J. Jurczak and S. Pikul, *Tetrahedron Lett.*, 26, 3039 (1985).
8. R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, 21, 478 (1956).
9. N. Minami, S. S. Ko, and Y. Kishi, *J. Am. Chem. Soc.*, 104, 1109 (1982).
10. J. Jurczak, S. Pikul, and K. Ankner, *Tetrahedron Lett.*, 27, 1711 (1986); S. Pikul, J. Raczko, K. Ankner, and J. Jurczak, *J. Am. Chem. Soc.*, 109, 3981 (1987).
11. W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, 43, 2923 (1978).
12. J. Jurczak, M. Chmielewski, and S. Filipek, *Synthesis*, 41 (1979).
13. R. W. Kierstead, A. Faraone, F. Mennona, J. Mullin, R. W. Guthrie, H. Crowley, B. Simko, and L. C. Blaber, *J. Med. Chem.*, 26, 1561 (1983).
14. E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, 128, 463 (1939).
15. J. Jurczak, T. Koźluk, S. Filipek, and C. H. Eugster, *Helv. Chim. Acta*, 65, 1021 (1982).