

Preparation of 2-deoxy-2-*C-p*-tolylsulfonyl- β -D-glucopyranosyl *p*-tolylsulfones having non-chair conformation and their elimination reactions

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^1H NMR and ^{13}C NMR data of all new compounds measured by Bruker Advance 400 (in CDCl_3 , otherwise cited) were assigned by ^1H NMR, COSY, NOESY, ^{13}C NMR, HMQC, and HMBC. Example spectra of **6** and **7** were separately enclosed.

Compound **3**; δ_{H} 6.16(1H, d, $J_{1,2}$ 3.5, H-1), 3.52(1H, dd, H-2), 5.52(1H, dd, $J_{2,3}$ 11.1, $J_{3,4}$ 9.4, H-3), 5.08(1H, dd, $J_{4,5}$ 9.7, H-4), 4.37(1H, ddd, $J_{5,6}$ 4.1, $J_{5,6'}$ 1.9, H-5), 4.33(1H, dd, $J_{6,6'}$ 12.4, H-6), 4.08(1H, dd, H-6'), 2.34(3H, s, SPhCH_3), 2.07(3H, s, OCOCH_3), 2.04(3H, s, OCOCH_3), 1.96(3H, s, OCOCH_3); δ_{C} 170.45(OCOMe), 169.80(OCOMe), 169.63 (OCOMe), 94.07(C-1), 56.28(C-2), 71.30(C-3), 68.63 (C-4), 70.97(C-5), 61.31(C-6), 21.06(SPhCH_3), 20.64 (OCOCH_3), 20.60 (OCOCH_3), 20.56 (OCOCH_3).

Compound **4**; δ_{H} 4.43(1H, d, $J_{1,2}$ 10.5, H-1), 2.71(1H, dd, H-2), 3.40(1H, ddd, $J_{2,3}$ 10.2, $J_{3,\text{OH-3}}$ 1.7, H-3), 3.56(1H, ddd, $J_{3,4}$ 8.7, $J_{4,5}$ 9.4, $J_{4,\text{OH-4}}$ 2.3, H-4), 3.19(1H, ddd, H-5), 3.83(1H, ddd, $J_{5,6}$ 3.5, $J_{6,6'}$ 11.9, $J_{6,\text{OH-6}}$ 6.7, H-6), 3.71(1H, ddd, $J_{5,6'}$ 5.8, $J_{6',\text{OH-6}}$ 6.4, H-6'), 3.20(1H, d, OH-3 at 3 position), 2.69(1H, d, OH-4), 2.36(3H, s, SPhCH_3), 2.33 (3H, s, SPhCH_3), 1.95(1H, t, OH-6); δ_{C} 86.50(C-1), 55.02(C-2), 74.46(C-3), 71.64(C-4), 78.74(C-5), 62.68(C-6), 21.20(SPhCH_3), 21.13 (SPhCH_3).

Compound **5**; δ_{H} 5.15(1H, d, $J_{1,2}$ 4.3, H-1), 4.11(1H, dd, $J_{2,3}$ 5.9, H-2), 4.30(1H, dt, $J_{3,4}$ 7.6, $J_{3,\text{OH}}$ 5.9, H-3), 4.02(1H, dd, $J_{4,5}$ 9.7, $J_{4,\text{OH}}$ 4.3, H-4), 3.67(1H, dt, $J_{5,6} = J_{5,6'}$ 3.8, H-5), 3.80(2H, bd, H-6, -6'), 3.58(1H, d, 3-OH), 2.98 (1H, d, 4-OH), 1.92 (1H, bs, 6-OH), 2.45(3H, s, SO_2PhCH_3), 2.30(3H, s, SO_2PhCH_3); δ_{C} 87.88(C-1), 65.44(C-2), 69.83(C-3), 69.01 (C-4), 78.61(C-5), 62.31(C-6), 22.10(SO_2PhCH_3 , SO_2PhCH_3).

Compound **6**; δ_{H} 5.39(1H, d, $J_{1,2}$ 2.7, H-1), 4.25(1H, dd, H-2), 5.64(1H, dd, $J_{2,3}$ 2.9, $J_{3,4}$ 6.2, H-3), 5.44(1H, dd, $J_{4,5}$ 9.7, H-4), 4.11(1H, ddd, $J_{5,6}$ 2.5, H-5), 4.38(1H, dd, $J_{5,6}$ 5.1, $J_{6,6'}$ 12.2, H-6), 4.05(1H, dd, H-6'), 2.48(3H, s, SO_2PhCH_3), 2.47(3H, s, SO_2PhCH_3), 2.07(3H, s, OCOCH_3), 2.05(3H, s, OCOCH_3), 1.86(3H, s, OCOCH_3); δ_{C} 170.37 (OCOMe), 169.44 (OCOMe), 169.21 (OCOMe), 6.26(C-1), 61.31(C-2), 67.43(C-3), 67.65(C-4), 73.50(C-5), 62.27(C-6), 21.77(SO_2PhCH_3), 21.73(SO_2PhCH_3), 20.66(OCOCH_3), 20.66(OCOCH_3), 20.41(OCOCH_3).

Compound **7**; δ_{H} (C_6D_6) 5.86(1H, d, $J_{1,2}$ 1.6, H-1), 5.46(1H, s, CHPh), 4.67(1H, dd, H-2), 4.72(1H, dd, $J_{2,3}$ 2.9, $J_{3,4}$ 8.3, H-3), 4.62(1H, dd, $J_{4,5}$ 10.2, H-4), 4.21(1H, dt, $J_{5,6a}$ 10.2, $J_{5,6e}$ 5.3, H-5), 3.63(1H, t, H-6a), 4.10(1H, dd, $J_{6a,6e}$ 10.2, H-6e), 1.90(3H, s, SO_2PhCH_3), 1.86(3H, s, SO_2PhCH_3); δ_{C} (C_6D_6) 102.01(CHPh), 87.29(C-1), 65.91(C-2), 67.32(C-3), 79.31(C-4), 66.88(C-5), 68.92(C-6), 21.21(SO_2PhCH_3), 21.20(SO_2PhCH_3).

Compound **8**; δ_{H} (C_6D_6) 7.54(1H, s, H-1), 4.59(1H, dd, $J_{3,4}$ 7.3, $J_{3,\text{OH-3}}$ 1.4, H-3), 3.93(1H, d, OH-3), 3.60(1H, dd, $J_{4,5}$ 10.3, H-4) 3.18(1H, dt, H-5), 3.29(1H, t, $J_{5,6a}$ 10.3,

$J_{6a,6e}$ 10.5, H-6a), 3.92(1H, dd, $J_{5,6e}$ 5.1, H-6e), 5.22(1H, s, CHPh), 1.98(3H, s, SO₂PhCH₃); δ_C (C₆D₆) 154.54(C-1), 119.53(C-2), 65.90(C-3), 79.38 (C-4), 69.97 (C-5), 67.31(C-6), 101.61(CHPh), 21.10(SO₂PhCH₃).

Compound **9**; δ_H (C₆D₆). 7.87(1H, s, H-1), 6.01(1H, dd, $J_{3,4}$ 3.2, $J_{3,5}$ 0.7, H-3), 5.19(1H, dd, $J_{4,5}$ 2.3, H-4), 4.26(1H, ddd, $J_{5,6'}$ 3.8, H-5), 4.32(1H, dd, $J_{5,6}$ 7.6, $J_{6,6'}$ 11.6, H-6), 3.87(1H, dd, H-6'), 1.88(3H, s, SO₂PhCH₃), 1.63(3H, s, OCOCH₃), 1.50(3H, s, OCOCH₃), 1.39(3H, s, OCOCH₃); δ_C (C₆D₆). 169.54(OCOMe), 168.62(OCOMe), 168.62(OCOMe), 155.28(C-1), 114.79(C-2), 62.01(C-3), 65.96(C-4), 75.45(C-5), 60.64(C-6), 21.02(SO₂PhCH₃), 19.96(OCOCH₃), 19.96(OCOCH₃), 19.72(OCOCH₃).

Compound **10**; δ_H 5.52(1H, d, $J_{1,2}$ 4.5, H-1), 4.29(1H, dd, H-2), 4.59(1H, dd, $J_{2,3}$ 9.7, $J_{3,4}$ 10.7, H-3), 4.32(1H, dd, $J_{4,5}$ 10.5, H-4), 3.99(1H, ddd, $J_{5,6}$ 4.6, $J_{5,6'}$ 2.4, H-5), 3.90(1H, dd, $J_{6,6'}$ 12.6, H-6), 3.80(1H, dd, H-6'), 3.40(3H, s, OCH₃), 3.22(3H, s, OCH₃), 2.47(3H, s, SO₂PhCH₃), 2.46(3H, s, SO₂PhCH₃), 1.75-1.26(8H, m, C₆H₈(OMe)₂); δ_C 87.11(C-1), 61.79(C-2), 66.01 (C-3), 63.44(C-4), 79.50(C-5), 62.20(C-6), 47.74(OCH₃), 47.05(OCH₃), 26.89(C₆H₈(OMe)₂), 26.63(C₆H₈(OMe)₂), 21.74(SO₂PhCH₃), 21.70(SO₂PhCH₃), 21.33(C₆H₈(OMe)₂), 21.21(C₆H₈(OMe)₂).

Compound **11**; δ_H (C₆D₆); 5.89(1H, d, $J_{1,2}$ 3.7, H-1), 4.78(1H, dd, H-2), 5.07(1H, dd, $J_{2,3}$ 9.2, $J_{3,4}$ 11.0, H-3), 4.79 (1H, dd, $J_{4,5}$ 10.3, H-4), 44.25(1H, ddd, H-5), 4.91(1H, dd, $J_{5,6}$ 7.6, $J_{6,6'}$ 12.1, H-6), 4.59(1H, dd, $J_{5,6'}$ 2.2, H-6'), 3.44(3H, s, OCH₃), 2.99(3H, s, OCH₃), 1.89(3H, s, SO₂PhCH₃), 1.85(3H, s, SO₂PhCH₃), 1.74(s, 3H, OCOCH₃), 1.42-1.27 (8H, m, C₆H₈(OMe)₂); δ_C (C₆D₆) 169.99(OCOMe), 87.96(C-1), 62.37(C-2), 66.38 (C-3), 65.12(C-4), 77.29(C-5), 64.34(C-6), 47.68(OCH₃), 46.61(OCH₃), 30.15(C₆H₈(OMe)₂), 29.77(C₆H₈(OMe)₂), 27.13(C₆H₈(OMe)₂), 27.02(C₆H₈(OMe)₂), 21.50(SO₂PhCH₃), 21.14(SO₂PhCH₃), 20.40(OCOCH₃).

Compound **12**; δ_H (C₆D₆); 7.53(1H, d, $J_{1,3}$ 1.4, H-1), 5.12(1H, dd, $J_{3,4}$ 9.2, H-3), 4.11 (1H, dd, $J_{4,5}$ 10.8, H-4), 3.59(1H, ddd, H-5), 4.34(1H, dd, $J_{5,6}$ 2.1, $J_{6,6'}$ 12.2, H-6), 4.08(1H, dd, $J_{5,6'}$ 4.3, H-6'), 3.41(3H, s, OCH₃), 2.68(3H, s, OCH₃), 1.91(3H, s, SO₂PhCH₃), 1.57(3H, s, OCOCH₃), 1.40-1.28 (8H, m, C₆H₈(OMe)₂); δ_C (C₆D₆) 165.68(OCOMe), 153.97(C-1), 117.60(C-2), 65.62(C-3), 65.26(C-4), 76.32 (C-5), 60.97(C-6), 47.07(OCH₃), 46.07(OCH₃), 30.16 (C₆H₈(OMe)₂), 28.45(C₆H₈(OMe)₂), 27.08(C₆H₈(OMe)₂), 26.87(C₆H₈(OMe)₂), 21.15(SO₂PhCH₃), 20.06(OCOCH₃).