Electronic Supplementary Information

Ionic hydrogenation of C-20, 22-ketene dithioacetal : stereoselective synthesis of steroidal C(20R) aldehydes

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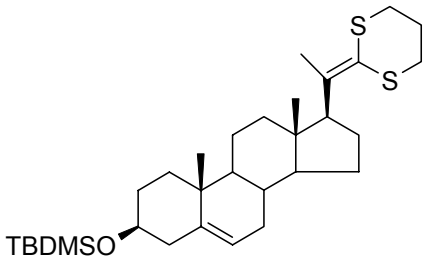
Contents.

General Experimental Procedure

All reagents were commercially obtained (Aldrich, Lancaster) at highest commercial quality and used without further purification except where noted. Air- and Moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 45 °C at approximately 20 mmHg. All non- aqueous reactions were carried out under anhydrous conditions using flame-dried glassware within an argon atmosphere in dry, freshly distilled solvents, unless otherwise noted. All melting points were determined on Yanco Micro melting point apparatus. Optical rotations were obtained on Bellingham and Stanly ADP-220 Polarimeter. Yields refer to chromatographically and spectroscopically (^{1}H NMR, ^{13}C NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) using TLC aluminium sheets, silica gel 60-F_{254} precoated, Merck, Germany and locating the spots using UV light as the visualizing agent or spraying with ethanolic phosphomolybdic acid (PMA) solution followed by heating. Flash column chromatography was carried out with silica gel (300-400 mesh). Preparative thin-layer chromatography separations were carried out on 2 mm E. Merck silica gel plates (60-F_{254}). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 MHz) at 200.13 and 50.32, or on a Bruker MSL-300 at 300.13 and 75.47 or on a Bruker DRX-500 spectrophotometer at 500.13 and 125.78 respectively. Chemical shifts are given in δ values relative to TMS (tetramethylsilane) as internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. IR spectra were recorded on Schimadzu

8400 series FTIR instrunent and values are reported in cm^{-1} units. Specific rotations ($[\alpha]_D$) are reported in deg/dm and the concentration (c) is given in g/100ml in the specific solvent. Mass spectra were recorded by either LC-MS or MS-TOF API QSTAR PULSAR spectrophotometer, samples introduced by infusion method using Electrospray Ionisation Technique. Elemental analysis were performed by CHNS-O EA 1108-Elemental anlyser, Carloerba Instument (Italy) or Elementor Vario EL (Germany) and were within $\pm$ 0.4% of calculated values. X-ray data were recorded on a Bruker SMART APEX CCD diffractometer.

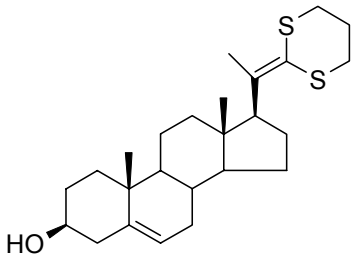
3β-*tert*-butyldimethylsilyloxy-pregna-5-en-20, 22-ketene-dithioacetal (10).



To the solution of 3β-*tert*-butyldimethylsilyloxy-(20*R*)-20-hydroxy-pregna-5-en-dithiane **9** (0.55 g, 1 mmol) in a mixture of dichloromethane (5 mL) and pyridine (10 mL) was cooled to –5 °C and a solution of $SOCl_2$ (4 mL) in dichloromethane (10 mL) was added dropwise under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 5 minutes. It was then quenched with crushed ice. The reaction mixture was extracted with dichloromethane (2 × 100 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded 0.52 g of crude product. Column chromatographic purification of crude product over silica gel using ethyl acetate-pet ether (1 : 99; Rf- 0.75, 5% EA/PE) as eluent gave **10** (0.46 g, 84%): pale yellowish solid ; 50 mg of this was crystallised from 2 ml of solvent (Dichloromethane-Methanol 3:7), mp 187-188 °C ; $[\alpha]_D^{25}$ –143.0 (c 0.61, $CHCl_3$); ^{1}H NMR (CDCl3, 200 MHz) δ = 5.32 (d, 1H, *J* = 6Hz, 6-H), 3.47 (m, 1H, 3-H), 2.89-2.94 (m, 4H, dithiane-CH_2), 1.86 (s, 3H, 21-H_3), 0.98 (s, 3H, 19-H_3), 0.87 (s, 9H, t-butyl CH_3), 0.62 (s, 3H, 18-H_3), 0.04 (s, 6H, $SiMe_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 141.58, 138.61, 122.95, 120.96 (CH), 72.52 (CH), 55.46 (CH), 53.95 (CH), 50.39 (CH), 46.75 (C), 42.78 (CH_2), 38.00 (CH_2), 37.89 (CH_2), 37.30 (CH_2), 31.94 (CH), 31.79 (CH_2), 30.5 (CH_2), 29.81 (CH_2), 28.5 (CH_2) , 25.91 (CH_2), 24.92 (CH_2), 20.65 (CH_2), 19.40 (CH_3), 18.78 (CH_3), 18.15 (CH_3), 14.11 (CH_3), 12.35 (CH_3), 4.60 (CH_3); MS (EI) m/z;

532, 477, 433, 366, 291, 227, 212, 186, 177, 125, 97, 75; IR (nujol, cm^{-1}) no peak at 3458; Anal. Calcd for $C_{31}H_{52}OS_2Si$: C 69.86; H 9.83; S 12.05; Found: C 69.88; H 9.92; S 11.58.

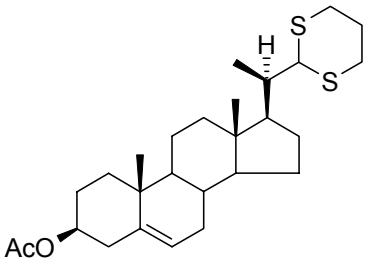
3β-hydroxy-pregna-5-en-20, 22-ketene-dithioacetal (11).



To a solution of 3β-*tert*-Butyldimethylsilyloxy-pregna-5, 20-dien-dithiane **10** (1.064 g, 2 mmol) in anhydrous THF (15 mL) and n-tetrabutyl ammonium fluoride in THF (4 mL, 4 mmol) was added and the reaction mixture was stirred at 30 °C for 18 h and then quenched with aqueous ammonium chloride. THF was removed under vaccuo and extracted with ethyl acetate (2 × 75 mL). The combined organic extracts were washed with brine (25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded 0.85 g of crude compound. Column chromatographic purification of crude product over SiO_2 using ethyl acetate-pet ether (20 : 80; Rf-0.4, 20% EA/PE) as eluent afforded **11** (0.78 g, 93%): colourless solid; 45 mg of this was crystallised from 2 ml of solvent (Ethyl acetate-Hexane 4:6), mp 115-116 °C (Ethyl acetate-Hexane 4:6); $[\alpha]_D^{27}$ – 46.57 (c 0.43, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.35 (d, 1H, *J* = 6 Hz, 6-H), 3.54 (m, 1H, 3-H), 2.87 (m, 4H, dithiane-CH_2), 1.84 (s, 3H, 21-H_3), 0.98 (s, 3H, 19-H_3), 0.62 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 140.49 (C), 138.29 (C), 122.59 (C), 121.09 (CH), 71.28 (CH), 55.07 (CH), 53.60 (CH), 50.00 (CH), 46.36 (C), 41.87 (CH_2), 37.43 (CH_2), 36.87 (CH_2), 36.27(C) , 31.51(CH_2) , 31.36 (CH_2), 31.25 (CH_2), 30.00 (CH_2), 29.45 (CH_2),

(CH_3), 20.61(CH_2) , 19.22 (CH_3), 18.63 (CH_3), 14.07(CH_3) ; IR (nujol, cm^{-1}) 1720; MS (LCMS) m/z: 478.04 (M+H_2O), 462.04 (M+1); Anal. Calcd for $C_{27}H_{40}O_2S_2$: C 70.38; H 8.75; S 13.917; Found C 70.70; H 7.80; S 14.31.

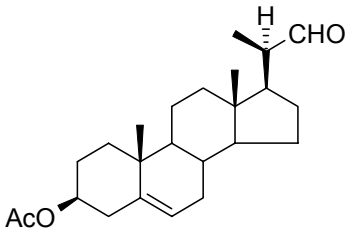
3β-acetoxy-pregna-5-en-20-dithiane (13).



To the solution of 3β-acetoxy-pregna-5, 20-dien-dithiane **12** (0.46 g, 1 mmol) in dichloromethane (10 mL), triethylsilane (0.16 mL, 1 mmol) and trifluoroacetic acid (0. 39 mL, 5 mmol) were sequentially added. The resulting red solution was stirred at 25 °C for 18 h, saturated sodium bicarbonate solution was added and the reaction was worked up with dichloromethane (2 × 75 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded 0.46 g crude product. Flash chromatographic purification over silica using ethyl acetate-pet ether (1 : 99; Rf- 0.53, 5% EA/PE tripple run) as a eluent afforded **13** (0.411 g, 89%); colourless solid; 63 mg of this was crystallised from 3 ml of solvent (Diethyl ether-Hexane 2:8), mp 175-176 °C ; $[\alpha]_D^{27.5}$ –32 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.38 (d, 1H, *J* = 6 Hz, 6-H), 4.62 (m, 1H, 3-H), 4.39 (d, 1H, *J* = 4 Hz, 22-H), 2.85 (m, 4H, dithiane-CH_2), 2.04 (s, 3H, $OCOCH_3$), 1.05 (d, 1H, *J* = 6Hz, 21-H_3), 1.03 (s, 3H, 19-H_3), 0.71 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 170.30 (C), 139.63 (C), 122.47 (CH), 73.86(CH) , 56.19 (CH), 55.54 (CH), 51.97 (CH), 50.08 (CH), 42.51 (C), 40.38 (CH), 38.91 (CH_2), 38.09 (CH_2), 36.56 (C), 36.09 (CH_2), 31.86 (CH), 31.77 (CH_2), 31.65

(CH_2), 30.61 (CH_2), 27.74 (CH_2), 27.16 (CH_2), 26.40 (CH_2), 24.02 (CH_2), 21.27 (CH_3), 21.06 (CH_2), 19.26 (CH_3) , 15.84 (CH_3) , 12.05 (CH_3); IR (nujol, cm^{-1}) 1730, 1236, 1045; MS (EI) m/z: 480.01 ($M+H_2O$), 464.02 (M+1); Anal. Calcd for $C_{27}H_{42}O_2S_2$: C 70.69; H 9.42; S 14.54%; Found C 70.07; H 9.14; S 13.85.

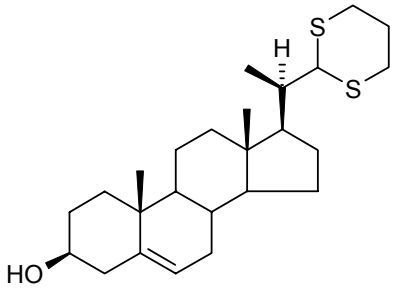
3β-acetoxy-pregna-5-en-22-aldehyde (4).



To a suspension of 3β-acetoxy-pregna-5-en-20-dithiane **13** (0.231 g, 0.5 mmol) in CH_3CN (5 mL) and H_2O (0.5 mL), HgO (0.16 g, 0.75 mmol) and $HgCl_2$ (0.27g, 1 mmol) were added. The reaction mixture was refluxed for 3 h with vigorous stirring. The solid mass was filtered through a pad of celite, residue was thoroughly washed with ethyl acetate. The reaction mixture was extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure gave a solid (0.2g) which was chromatographed over SiO_2 using ethyl acetate-pet ether (30 : 70; Rf- 0.42, 10% EA/PE) as an eluent afforded compound **6** (0.18 g, 96%): colourless solid; 33 mg of this was crystallised from 2 ml of solvent (Ethyl acetate-Hexane 3:7), mp 118-120 °C, (Lit[1] 120-121 °C) $[\alpha]_D^{24.6}$ –57.14 (c 0.385, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ = 9.55 (d, 1H, *J* = 5 Hz, CHO), 5.38 (d, 1H, *J* = 6 Hz, 6-H), 4.60 (m, 1H, 3-H), 2.03 (s, 3H, $OCOCH_3$), 1.03 (d, 1H, *J* = 6Hz, 21-H_3), 1.01 (s, 3H, 19-H_3), 0.69 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 205.58 (CH), 170.43 (C), 139.84(C) , 122.33 (CH), 73.90 (CH), 56.24 (CH),

51.97(CH) , 50.11 (CH), 48.78 (CH), 42.17 (CH), 38.46 (C), 38.14 (C), 37.04 (CH_2), 31.88 (CH_2), 31.82 (CH), 29.68 (CH_2), 27.78 (CH_2), 26.45 (CH_2), 23.91 (CH_2), 21.35 (CH_3), 20.76 (CH_2), 19.27 (CH_3), 13.52 (CH_3), 12.83 (CH_3); IR (nujol, cm^{-1}) 2960, 1730, 1710, 1247; MS (LCMS) m/z: 391.02, ($M+H_2O$), 373.03 (M+1), 313.03. Anal. Calcd for $C_{24}H_{36}O_3$: C 77.37; H 9.74; Found C 77.13; H 9.83.

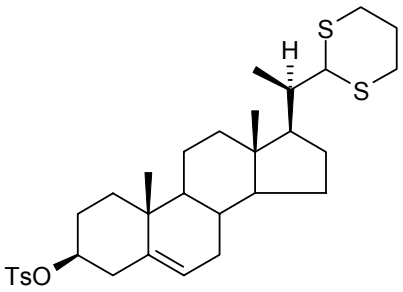
3β-hydroxy-pregna-5-en-20-dithiane (14).



To a stirred solution of 3β-acetoxy-pregna-5-en-20-dithiane **13** (0.231 g, 0.5 mmol) in methanol (5 mL) and THF (2 mL) was added aqueous solution of KOH (0.14g, 2.25 mmol) in H_2O (0.5 mL). The reaction mixture was stirred at 30 °C for 4 h. It was quenched with water (10 mL), methanol and THF was removed under reduced pressure and the residue was extracted with ethyl acetate (2 × 100 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure yielded 3β-hydroxy-pregna-5-ene-20-dithiane **14** (0.193, 92%); colourless solid; 38 mg of this was crystallised from 2 ml of solvent (Ethyl acetate-Hexane 4:6), mp 184-185 °C; $[\alpha]_D^{25}$ -32 (c = 0.75, $CHCL_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.35 (d, 1H, *J* = 6 Hz, 6-H), 4.39 (d, *J* = 4 Hz, 1H, 22-H), 3.54 (m, 1H, 3-H), 2.84 (m, 4H, dithiane -CH_2), 2.30 (d, 2H, 4-H), 1.05 (d, 3H, *J* = 6 Hz, 21-H_3), 1.02 (s, 3H, 19-H_3), 0.71 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 140.74 (C), 121.63

(CH), 71.75 (CH), 56.30 (CH), 55.59 (CH), 52.01 (CH), 50.20 (CH), 42.55 (C), 42.31 (CH_2), 40.46 (CH), 39.03 (CH_2), 37.27 (CH_2), 36.51 (C), 31.93 (CH), 31.82 (CH_2), 31.71 (CH_2), 31.67 (CH_2), 30.66 (CH_2), 27.27 (CH_2), 26.45 (CH_2), 20.48 (CH_2), 21.17 (CH_2), 19.40 (CH_3), 15.95 (CH_3), 12.10 (CH_3). IR (nujol, cm^{-1}); 3310; MS (LCMS) m/z: 438.02 ($M+H_2O$), 422.02(M+2). Anal. Calcd for $C_{25}H_{40}OS_2$: C 71.37; H 9.58; S 15.24; Found C 71.17; H 9.62; S 15.15.

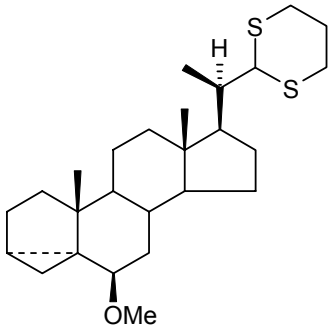
3β-tosyl-pregna-5-en-20-dithiane (15).



To a solution of 3β-hydroxy-pregna-5-en-20-dithiane **14** (0.19 g, 0.45 mmol) in pyridine (2 mL) was added p-toluenesulfonyl chloride (430 g, 2.25 mmol) and the reaction mixture was kept in the dark for a period of 12 h. It was then slowly poured to an ice cold saturated solution of $NaHCO_3$ (5 mL) and was kept for 1 h with occasional stirring. The reaction mixture was extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded compound **15** (0.243 g, 94%); pale crystalline solid; mp 70-71 °C; ^{1}H NMR ($CDCl_3$; 500 MHz) δ = 7.80 (d, 2H, *J* = 10 Hz), 7.33 (d, 2H, *J* = 10 Hz), 5.29 (d, 1H, *J* = 5 Hz, 6-H), 4.37 (d, 1H, *J* = 5 Hz, 22-H), 4.32 (m, 1H, 3-H), 2.82 (m, 4H, dithiane -CH_2), 2.45 (s, 3H, Ar-CH_3), 1.04 (d, 3H, *J* = 5 Hz, 21-H_3), 0.97 (s, 3H, 19-H_3), 0.68 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 200 MHz) δ = 144.38 (C), 138.86 (C),

129.71 (C), 127.58 (C), 123.39 (CH), 82.26 (CH), 56.12 (CH), 55.57 (CH), 51.86 (CH), 49.84 (CH), 42.45 (C), 42.3 (CH_2), 40.39 (CH), 38.81 (CH_2), 36.79 (CH_2), 36.27 (C), 31.68 (CH_2), 30.61 (CH_2), 29.84 (CH_2), 28.59 (CH_2), 27.19 (CH_2), 26.35 (CH_2), 24.00 (CH_2), 21.57 (CH_2), 21.02 (CH_3), 19.11 (CH_3), 15.95 (CH_3), 12.05 (CH_3). IR (nujol, cm^{-1}); no peak at 3500, 2400, 1216.37.

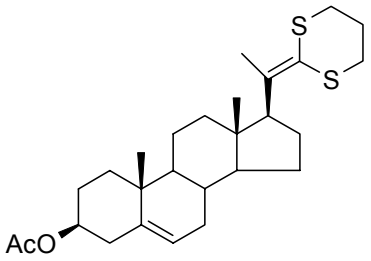
3α, 5-Cyclo-6β-methoxy-pregna-20-dithiane (16).



To a solution of 3β-tosyl-pregna-5-en-20-dithiane **15** (0.2 g, 0.35 mmol) in dry methanol (3 mL), fused potassium acetate (0.172 g, 1.75 mmol) was added and the reaction mixture was refluxed for a period of 4 h. Methanol was evaporated under reduced pressure and the gummy mass was extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded crude i-methyl ether 18 (0.18 g). Preparative thin layer chromatographic purification (Rf- 0.75, 10% EA/PE) afforded the pure i-methyl ether **16** (0.125 g, 83%): foam; mp118-120 °C; $[\alpha]_D^{25}$ + 5.74 (c 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 4.40 (d, 1H, *J* = 6 Hz, 22-H), 3.32 (s, 3H, -OCH $_3$), 2.97 (t, 1H, 6-H), 2.83 (m, 4H, dithiane -CH_2), 1.05 (d, 3H, *J* = 5 Hz, 21-H_3), 1.03 (s, 3H, 19-H_3), 0.75 (s, 3H, 18-H_3), 0.65 (t, 1H, *J* = 10 Hz), 0.44 (dd, 1H, *J* = 10 and 10 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 82.43 (CH), 56.55 (CH), 56.17 (CH), 55.65 (CH), 52.18

24.56(CH_2) , 20.33 (CH), 18.97 (CH_3), 18.35 (CH_3), 13.72 (CH_3); IR (nujol, cm^{-1}) 3315 (-OH); MS (EI) m/z: 418 (M^+), 403, 343.; Anal. Calcd for $C_{25}H_{38}OS_2$: C 71.71; H 9.148; S 15.314; Found: C 71.63; H 9.21; S 15.34.

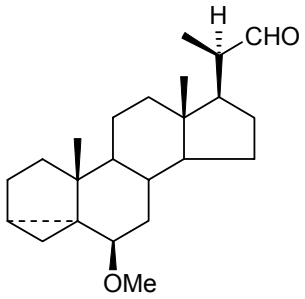
3β-acetoxy-pregna-5-en-20, 22-ketene-dithioacetal (12).



To the solution of 3β-hydroxy-pregna-5, 20-dien-dithiane **11** (0.75 g, 1.8 mmol) in pyridine (4 mL) was added acetic anhydride (1.7 mL, 18 mmol) and N,N-dimethylaminopyridine (0.031 g, 0.25 mmol). The reaction mixture was stirred at 30 °C for 3 h. The reaction was quenched with crushed ice and extracted with ethyl acetate (2 × 100 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure afforded crude product (0.83 g). Column chromatographic purification over SiO_2 using ethyl acetate-pet ether (2 : 98; Rf- 0.66, 15%EA/PE) as eluent afforded **12** (0.81g, 98%): colourless solid; 48 mg of this was crystallised from 2 ml of solvent (Ethyl acetate-Hexane 1:9), mp 159-160 °C ; $[\alpha]_D^{27.6}$ – 141.17 (c 0.51, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.38 (d, 1H, *J* = 6 Hz, 6-H), 4.61 (m, 1H, 3-H), 2.93 (m, 4H, dithiane-CH_2), 2.02 (s, 3H, $OCOCH_3$), 1.85 (s, 3H, 21-H_3), 0.99 (s, 3H, 19-H_3), 0.62 (s, 3H, 18-H_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 170.18 (C), 139.78 (C), 138.24 (C), 123.20 (C), 122.40 (CH), 73.84 (CH), 55.39(CH) , 53.92 (CH), 50.31 (CH), 46.67 (C), 38.07 (CH_2), 37.85 (CH_2), 36.97 (CH_2), 36.68 (C), 31.90 (CH_2) , 31.79 (CH), 30.32 (CH_2), 29.73 (CH_2), 27.71 (CH_2), 24.91 (CH_2), 21.20

(CH), 48.12 (CH), 43.45 (C), 43.01 (C), 40.51 (CH), 39.48 (CH_2), 35.38 (CH_2), 35.06 (CH), 33.42 (CH_2), 31.74 (CH_2), 30.69 (CH_2), 30.55 (CH), 27.38 (CH_2), 26.49 (CH_2), 24.97 (CH_2), 24.01 (CH_2), 22.88 (CH_2), 21.55 (CH_3), 19.27 (CH_3), 15.93 (CH_3), 13.09 (CH_2), 12.51 (CH_3); IR (nujol, cm^{-1}); 1215.07; MS (LCMS) m/z: 451.99 ($M+H_2O$); Anal. Calcd for $C_{26}H_{40}OS_2$: C 71.83; H 9.73; S 14.75; Found C 71.78; H 9.82; S 14.57.

3α, 5-Cyclo-6β-methoxy-pregna-22-aldehyde (6).



To a solution of **3**α, 5-Cyclo-6β-methoxy-pregna-20-dithiane **16** (0.043 g, 0.1 mmol) in 1 mL of 8 : 1 : 1 MeCN/CH_2Cl_2/H_2O was added Dess-Martin periodinane (0.085 g, 0.2 mmol) in one portion. The reaction mixture was stirred at room temperature, exposed to air, for 5 h. The reaction was quenched with 5 mL of 50% $NaHCO_3$ and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with brine (2 × 25 mL), dried over Na_2SO_4, concentrated under reduced pressure followed by purification of the product by preparative thin layer chromatography affords (0.02 g, 55%) the desired C-22 aldehyde **4** as a gum. $[\alpha]_D^{27}$+ 42.97 (c 0.605, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ = 9.55 (d, 1H, *J* = 6 Hz, CHO), 3.33 (s, 1H, OCH_3), 1.03 (d, 3H, 21-H_3), 1.01 (s, 3H, 19-H_3), 0.73 (s, 3H, 18-H_3).

Reference for Supplementary Information

(1) Sucrow, W.; Nooy, M. V. *Liebigs Ann. Chem.* **1982**, 1897-1906 and references cited theirin.

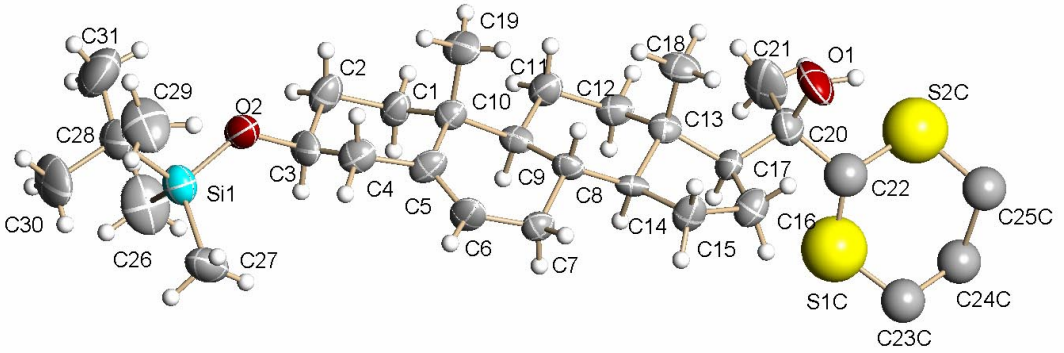


Figure. ORTEP view of 3β-*tert*-butyldimethylsilyloxy-(20*R*)-20-hydroxy-pregna-5-en-dithiane **9**

Rotational Disorder of Dithiane. Structure Solution of compound 9:

The structure of **9** was solved by Direct Methods Program SHELXS-97 (G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997). All the Non-H atoms could be located in the E-map, excepting those belonging to the dithiane ring. Repeated cycles of Least-squares refinement and Difference Fourier also did not contain the peaks corresponding to the atoms of this ring. Very low peak heights (~2 e $Å^{-3}$) always appeared for the two S atoms of the ring. This behavior, taking into account all the chemical evidence confirming the presence of the dithiane ring, was interpreted as extensive rotational disorder of the moiety about the C- bond (Figure 2).

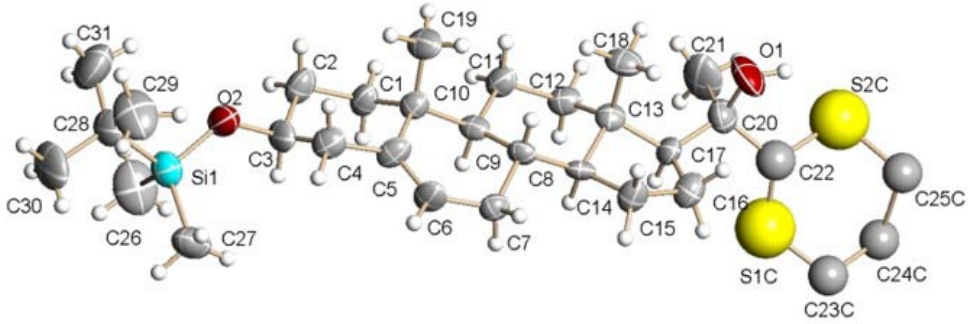


Figure 2

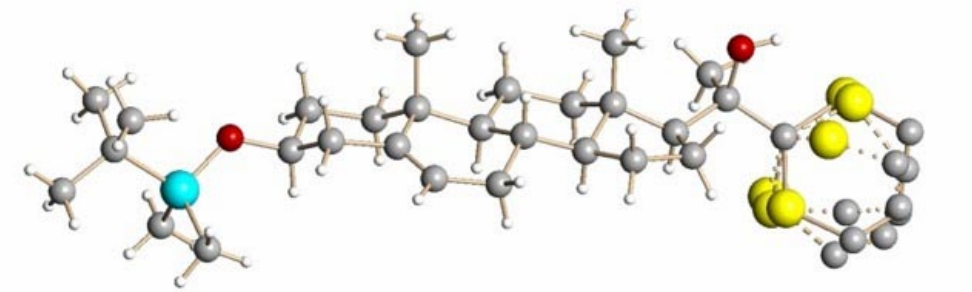


Figure 3

Disorder to the Dithiane Ring:

The peaks of the difference Fourier were modeled as rotational disorder of the dithiane about Cm - Cn bond; three conformers with 1/3 occupancy (Figure 2) could be identified with some difficulty. The extent of disorder could be more but we have normalized it over three major conformers. The R factor lowered from ~10% to ~8% and the isotropic temperature factors of the rings were reasonable. The packing of molecules () shows that the rotational disorder for dithiane is possible. The Si group which, comes close to dithiane also has higher thermal anisotropies. In the absence of any specific Hydrogen bonding and with the void present in the lattice, the model proposed for the disorder is justifiable.

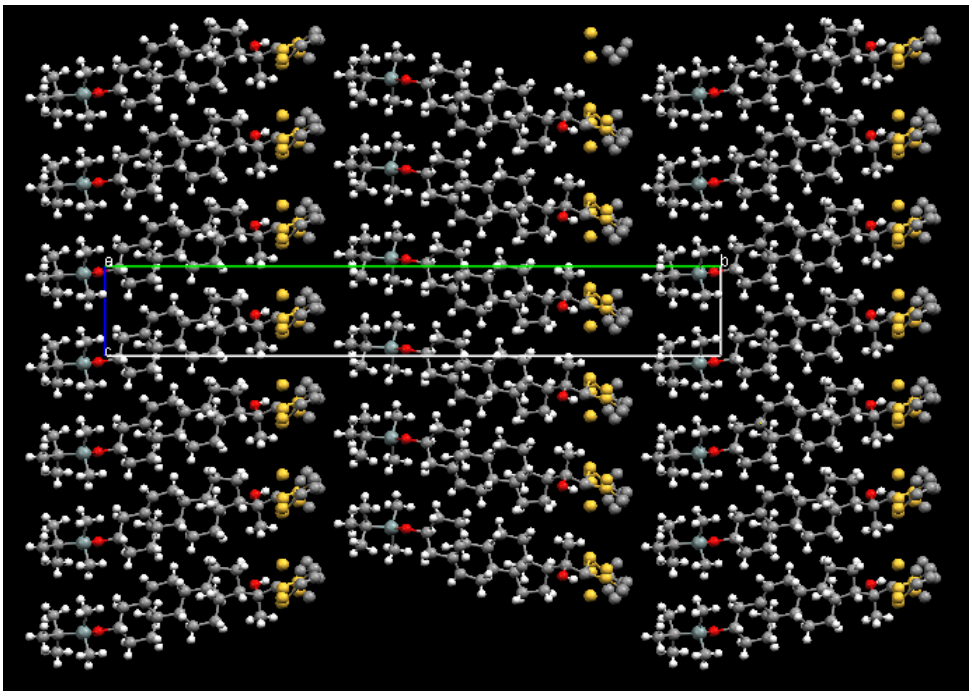


Figure 4

Restrained Least-Squares Refinement:

The least-squares refinement of the disordered dithiane was carried out as follows,

(a) Use of average geometrical parameters for the dithiane from CCDC,

(b) Use the constraints on the Geometrical parameters for position A of the ring,

(c) Use the SAME geometrical constraints for positions B and C,

(d) Use PARTS 1, 2 and 3 for refining the three positions of the ring with 1/3 occupancy except for the common atom C20 that has a full occupancy.

Crystal data for Compound 9

Single crystals of both **9** could be obtained from methanol-dichloromethane mixture . X-ray intensity data were collected on a Bruker SMART APEX CCD diffractometer at room temperature.

Crystal data for **9.** C_{31} H_{54} O_2 S_2 Si, M = 550, crystal dimensions 0.24 x 0.04 x 0.020 mm, crystal system: Monoclinic, space group $P\ 2_1$, a = 6.287(4), b = 41.68(3), c = 6.537(4) Å, β = 110.537(11)°, V= 1604.2(17) Å^3, Z = 2, D_c = 1.141 g cm^{-3},μ (Mo-K_α) = 0.228 mm^{-1}, T = 293(2) K, F(000) = 604, Max. and min. transmission 0.9955 and 0.9473, 11540 reflections collected, 5556 unique [I>2σ (I)], S= 0.958, R value 0.0826, $wR2$ = 0.1439 (all data *0.2387*, $wR2$ = 0.1958).

All the data were corrected for Lorentzian, polarisation and absorption effects using Bruker's SAINT and SADABS programs. SHELX-97 (G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997) was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model.