A Convenient Method for Retro-Cycloaddition of Adducts from Steroidal 5,7-Dienes and 4-Phenyl-1,2,4-triazolidine-3,5-dione and Application to the Syntheses of Biosynthetic Intermediates of Ergosterol

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Use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in boiling xylene was found to be a convenient method for the retro-cycloaddition of adducts of 4-phenyl-1,2,4-triazolidine-3,5-dione (PTAD) with steroidal 5,7-dienes. This process was applied to the syntheses of ergosta-5,7,24(28)-trien-3β-ol and ergosta-5,7,22,24(28)-tetraen-3β-ol.

Key words retro-cycloaddition; protection–deprotection; steroidal 5,7-diene; 4-phenyl-1,2,4-triazolidine-3,5-dione; 1,8-diazabicyclo[5.4.0]undec-7-ene

Protection of the unstable steroidal 5,7-diene system is an important process in steroid-vitamin D chemistry. The dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) is a good protecting group, since it provides 1,4-cycloadducts quantitatively, although a retro-cycloaddition process is necessary to remove the protecting group. Many methods to regenerate the 5,7-diene system have been developed. However, reducing agents such as $LiAlH_4$[1] or diisobutylaluminum hydride (DIBAL),[2] can not be employed for compounds having functional groups sensitive to hydride reduction. Use of dimethyl sulfoxide (DMSO)–K_2CO_3[3] or KOH–EtOH[4] is not possible for compounds unstable under basic conditions. To avoid these disadvantages, organic bases such as 1,3-dimethyl-2-imidazolidinone (DMI)[5] or γ-collidine,[6] have been used for retro 1,4-addition of the adducts, but they are available only when used as solvent, which make the purification process troublesome.

In the course of our continuous study on syntheses of active forms of vitamin D derivatives,[7] it was found that 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in refluxing xylene is a useful agent for the retro-cycloaddition of adducts bearing a variety of functional groups in the molecule. The results are shown in Table 1. Regeneration of the 5,7-diene system of the adducts from 1α,2α-epoxy-5,7-dienes and PTAD is also achieved in good yields to give the corresponding 1α,2α-epoxy-5,7-diene compounds which are useful intermediates[8] for introducing substituents at the C-2β position under alkaline conditions (Table 2).

The method described here is useful for synthesis of vitamin D derivatives because of its simplicity and the high yields, obtained as well as its applicability to compounds having groups sensitive to reducing, acidic and alkaline agents.

As an application of this process, the biosynthetic intermediates of ergosterol, ergosta-5,7,24(28)-trien-3β-ol (**17**)[9] and ergosta-5,7,22,24(28)-tetraen-3β-ol (**18**)[10] were synthesized by reaction of the C-22 iodide derivative (**9**)[11] or the C-20 aldehyde (**10**)[12] with the phenylsulfone derivative (**8**) as a common intermediate to generate the side chain moiety.

Thus, condensation of **9** in the presence of *n*-BuLi and DMI with **8** derived from the known phenyl sulfone (**1**) and epoxy alcohol (**2**),[13] and reduction of the product with 5% Na–Hg in methanol saturated with Na_2HPO_4, afforded the 28-ol (**11**). Tosylation of **11** and subsequent treatment with NaI in the usual manner gave 28-iodide derivative (**13**). Treatment of **13** with DBU in boiling xylene and deprotection of the *tert*-butyldimethylsilyl group with *n*-Bu_4NF in tetrahydrofuran (THF) produced the triene derivative (**17**). Similar treatment of **10** derived from ergosterol, in place of **9** afforded the tetraene derivative (**18**) as shown in Charts 1 and 2. The ergosterol derivatives obtained here are important compounds for biosynthetic study of ergosterol and its biosynthetic derivatives such as 22,23-dihidroergosterol (pro vitamin D_4)[14] and 24-*epi*-22,23-dihidroergosterol (pro vitamin D_7).[15]

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. ^{1}H-NMR spectra were taken in $CDCl_3$ on a JEOL-FX400 spectrometer with tetramethylsilane (TMS) as an internal standard. UV spectra were recorded on a Hitachi 320 spectrometer. Mass spectra were measured on a Hitachi M-80 spectrometer. Optical rotations were measured on a JASCO DIP 370 polarimeter. Solvents were dried over anhydrous magnesium sulfate and evaporated under reduced pressure.

A Typical Procedure for the Retro-Cycloaddition (Entry 2 in Table 2) A xylene solution (10 ml) of 1α,2α-epoxy-5α,8α-(4-phenyl-3,5-dioxo-1,2,4-triazolidine)-6-cholestene-3β,25-diol[8] (1.0 g, 1.7 mmol) and DBU (0.5 g, 3.4 mmol) was refluxed for 1.5 h with stirring. The solution was washed with brine and concentrated. The residue was purified by silica gel column chromatography (chloroform–ethyl acetate, 4 : 1, v/v) to afford 1α,2α-epoxy-5,7-cholestadiene-3β,25-diol (625 mg, 89%) as a foam. MS *m/z*: 414 (M^+). UV λ_{max}^{EtOH} nm (ε): 282 (11000). ^{1}H-NMR ($CDCl_3$) δ: 0.64 (3H, s, 18-CH_3), 0.97 (3H, d, J=6.4 Hz, 21-CH_3), 1.05 (3H, s, 19-CH_3), 1.22 (6H, s, 26,27-CH_3), 3.05 (1H, d, J=3.4 Hz, 1-H), 3.32 (1H, d, J=3.4 Hz, 2-H), 3.92 (1H, m, 3-H), 5.40, 5.71 (each 1H, m, 6-H, 7-H).

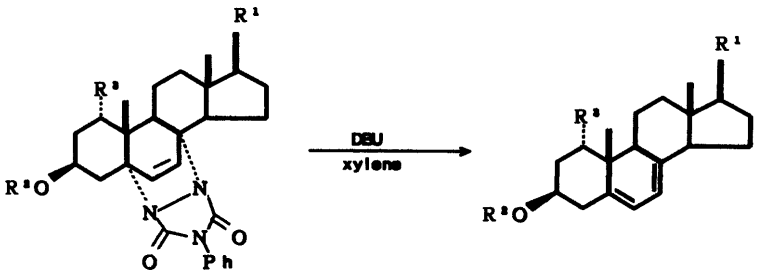
Treatment of the product with PTAD afforded the starting material quantitatively.

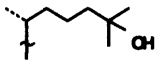
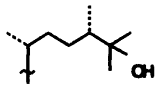
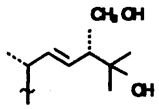
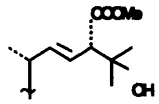
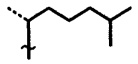
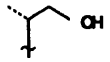
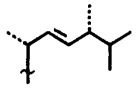
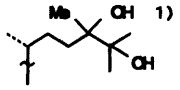
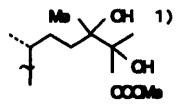
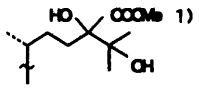
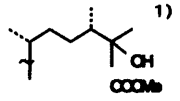
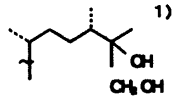
3-Methyl-2-(phenylsufonylmethyl)butane-1,3-diol (3) A chloroform solution (200 ml) of prenol (17 g, 0.2 mol) and *m*-chloroperbenzoic acid (*m*-CPBA) (43 g, 0.25 mol) was stirred at room temperature overnight. The solution was washed with 10% K_2CO_3 solution and brine, dried and concentrated. The residue was distilled (50—55 °C/5—7 mmHg) to give **2**[21] (13.4 g, 65%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.32, 1.36 (each 3H, s, 3-CH_3), 2.97—3.00 (1H, m, 2-H), 3.69, 3.85 (each 1H, m, 1-CH_2).

To a THF solution (500 ml) of **1** (15.6 g, 0.1 mol) and **2** (10.2 g, 0.1 mol), was added 1.6 M *n*-BuLi hexane (150 ml) solution at 0—10 °C. The solution was then stirred at room temperature overnight. After saturated NH_4Cl solution was added, the solution was extracted with ethyl acetate, washed with brine and concentrated. The residue was purified by silica gel chromatography. Elution with chloroform–ethyl acetate (1 : 1, v/v) afforded **3** (17.5 g, 68%) as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.16, 1.26 (each 3H, s, 3-CH_3), 2.17 (1H, m, 3-H), 2.55, 2.60 (each 1H, m, OH, disappeared with D_2O), 4.01 (2H, m, CH_2SO_2Ph), 7.54—7.95 (5H, m, C_6H_5).

3-Methyl-2-(phenylsulfonylmethyl)-3-buten-1-ol (6) To a pyridine solution of **3** (10.0 g, 39 mmol) was added benzoyl chloride (5.6 g, 40 mmol).

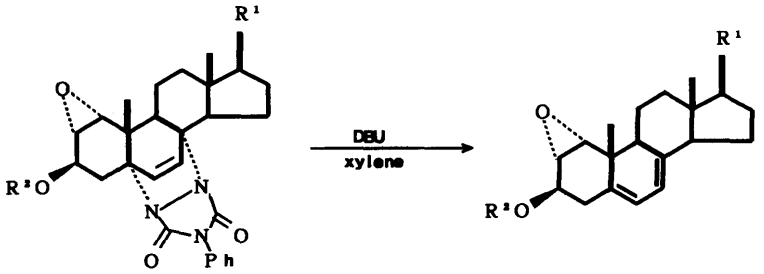
Table 1. Retro-Cycloaddition of PTAD Adduct of Steroidal 5,7-Dienes

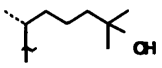
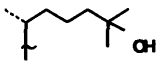
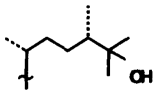
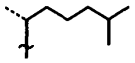
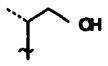


Entry	R^1	R^2	R^3	Yield (%)	Lit.
1		H	OH	86	7
2		Ac	OAc	86	11
3		H	H	83	12
4		H	H	85	12
5		H	OH	87	17
6		*tert*-$BuMe_2Si$	H	90	18
7		Ac	OAc	91	19
8		Ac	OAc	88	20
9		*tert*-$BuMe_2Si$	H	86	
10		*tert*-$BuMe_2Si$	H	80	
11		*tert*-$BuMe_2Si$	H	82	
12		*tert*-$BuMe_2Si$	H	82	
13		*tert*-$BuMe_2Si$	H	88	

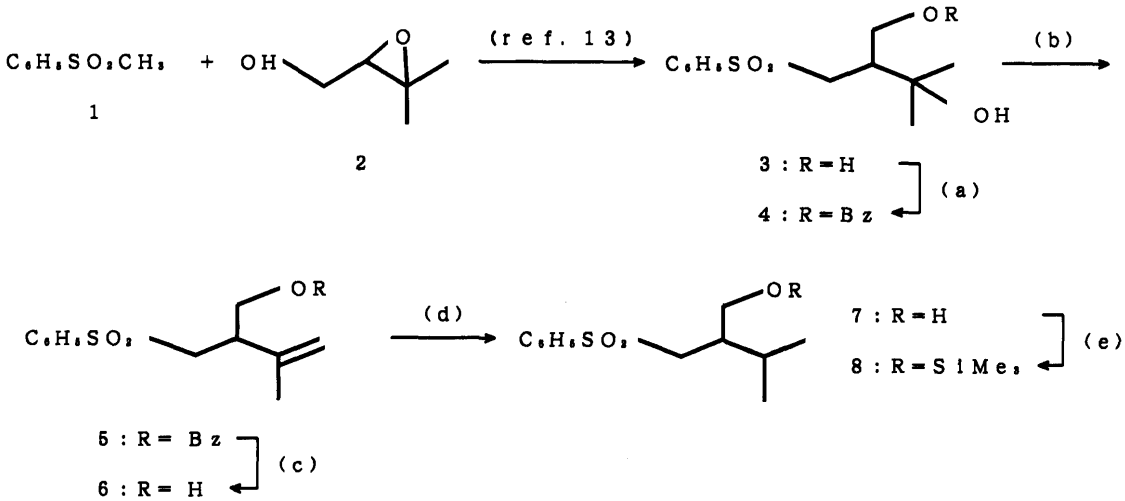
Conditions: reaction time (1.5 h), PTAD adducts/DBU (1/2). 1) Compounds (entry 9—13) are diastereomeric mixtures.

Table 2. Retro-Cycloaddition of PTAD Adducts of 1α,2α-Epoxy-steroidal 5,7-Dienes



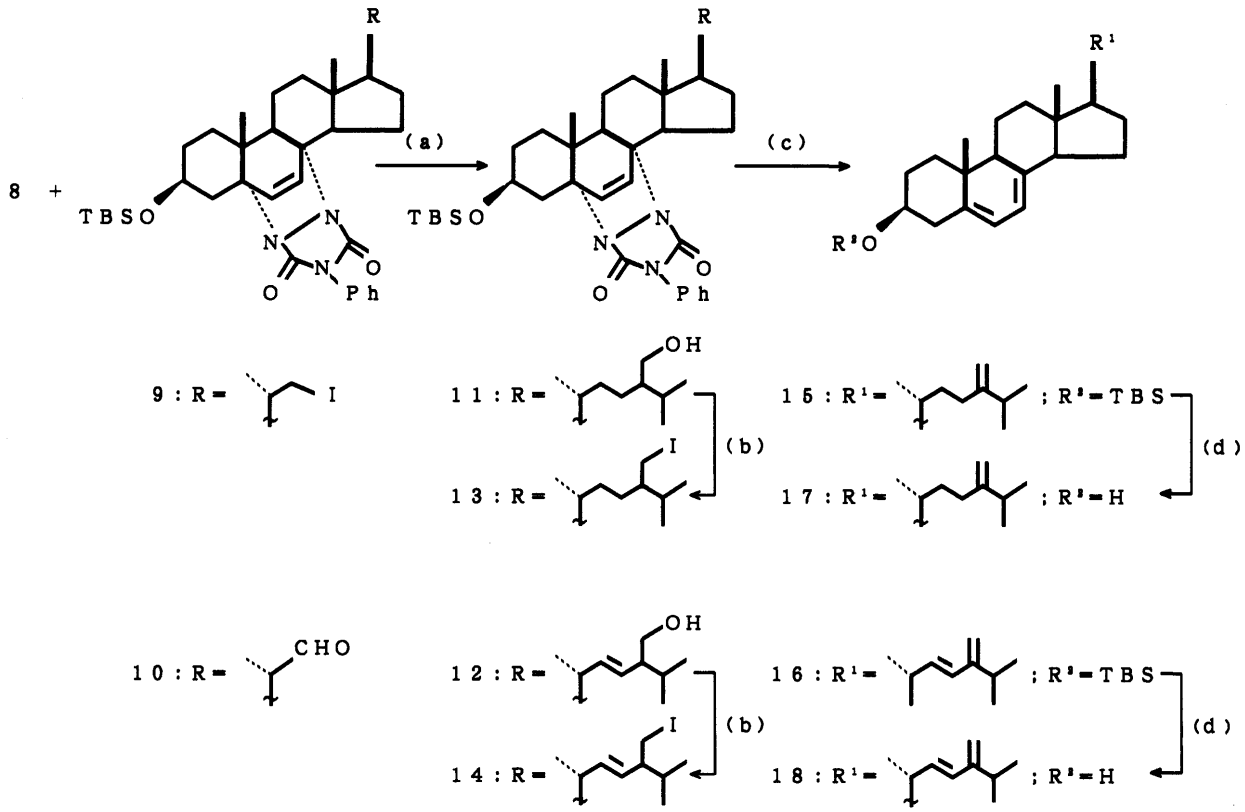
Entry	R^1	R^2	Yield (%)	Lit.
1		*tert*-$BuMe_2Si$	89	11
2		H	82	11
3		Bz	85	16
4		*tert*-$BuMe_2Si$	90	17
5		*tert*-$BuMe_2Si$	88	19
6		*tert*-$BuMe_2Si$	90	20

Conditions: reaction time (1.5 h), PTAD adduct/DBU (1/2).



(a) BzCl, pyridine, 4: 86%; (b) $MeSO_2Cl$, Et_3N, **5**: 77%; (c) KOH, EtOH, **6**: 75%; (d) H_2, Pd–C, MeOH, **7**: 100%; (e) Me_3SiCl, imidazole, DMF, 8: 75%.

Chart 1



(a) 1) *n*-BuLi, DMI; 2) 5% Na–Hg, Na_2HPO_4, **11**: 70%, **12**: 56%; (b) 1) TsCl, pyridine; 2) NaI, acetone, **13**: 86%, **14**: 40%; (c) DBU, xylene, **15**: 61%, **16**: 75%; (d) *n*-Bu_4NF, THF, **17**: 86%, **18**: 80%.

Chart 2

The mixture was stirred at room temperature for 5 h and extracted with ethyl acetate, washed with 10% HCl solution, saturated $NaHCO_3$ solution and brine. After the solution was concentrated, the residue was purified by silica gel chromatography. Elution with chloroform afforded **4** (12.1 g, 86%) as a colorless oil.

To an ether solution (600 ml) of **4** (10.0 g, 27 mmol) and methanesulfonyl chloride (10.0 g, 87 mmol), triethylamine (100 ml) was added at 0 °C. The mixture was stirred at 0 °C for 5 h and overnight at room temperature. After the solution was concentrated, the residue was extracted with ethyl acetate and washed with 10% HCl solution, saturated $NaHCO_3$ solution and brine. Evaporation of ethyl acetate and silica gel chromatography (chloroform) of the residue gave **5** (7.2 g, 77%) as a colorless oil.

To an ethanol solution (50 ml) of **5** (7.0 g, 20 mmol), 20% KOH–ethanol solution (50 ml) was added and the mixture was stirred for 1 h at room temperature. Water was added and the mixture was extracted with ethyl acetate. The solution was washed with brine, dried and concentrated. The residue was purified by silica gel chromatography (hexane–ethyl acetate, 1 : 4, v/v) to afford **6** (3.6 g, 75%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.66 (3H, s, 3-CH_3), 2.85 (1H, m, 2-H), 3.21—3.42 (2H, m, CH_2SO_2Ph), 3.70—3.74 (2H, m, 3-CH_2), 7.58—7.92 (5H, m, C_6H_5).

3-Methyl-2-(phenylsulfonylmethyl)-1-trimethysilyloxybutane (8) A methanol solution (30 ml) of **6** (7.2 g, 30 mmol) and 5% Pd–C (1.5 g) was hydrogenated at ordinary pressure and room temperature for 2 d. The mixture was filtered on Celite and the filtrate concentrated to dryness to give **7** (7.2 g, 100%) as a pale yellow oil.

A *N*,*N*-dimethylformamide (DMF) solution (35 ml) of **7** (7.1 g, 30 mmol), imidazole (5.4 g, 80 mmol) and trimethylsilyl chloride (4.3 g, 40 mmol) was stirred at 55 °C for 1 h. The mixture was then extracted with ethyl acetate. The solution was washed with brine and concentrated. The residue was chromatographed on silica gel (hexane–ethyl acetate, 9 : 1, v/v) to give **8** (7.1 g, 75%) as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.83—0.86 (6H, m, 3-CH_3), 1.86 (1H, m, 3-H), 2.02 (1H, m, 2-H), 3.05—3.26 (2H, m, CH_2SO_2Ph), 3.65—3.71 (2H, m, CH_2OSi), 7.60—7.96 (5H, m, C_6H_5).

3′,5′-Dioxo-4′-phenyl-3β-(*tert*-butyldimethylsilyloxy)-5α,8α[1′,2′]-1′,2′,4′-triazolidino-6-ergosten-28-ol (11) A THF solution (60 ml) of **8** (6.4 g, 20 mmol) was cooled to −60 °C and 1.6 M *n*-BuLi hexane solution (15 ml) was added and the mixture stirred for 30 min at the same temperature under a nitrogen atmosphere. After the addition of DMI (15 ml), a THF solution (50 ml) of **9** (7.3 g, 10 mmol) was added at −60 °C. The mixture was then stirred at −20 °C for 1 h. After addition of saturated NH_4Cl solution, the mixture was extracted with ethyl acetate, washed with brine, dried and evaporated. The residue was dissolved in THF (50 ml)–methanol (50 ml) and 5% Na–Hg (50 g) and Na_2HPO_4 (3 g) added. The mixture was stirred at room temperature under a nitrogen atmosphere overnight. After separation of Hg, the solution was concentrated, extracted with ethyl acetate, washed with brine and evaporated. The residue was purified by silica gel chromatography (chloroform–ethyl acetate, 9 : 1, v/v) to afford **11** (4.9 g, 70%) as an amorphous solid, which was employed without further purification. ^{1}H-NMR ($CDCl_3$) δ: 0.08, 0.10 (each 3H, s, Si-CH_3), 0.79 (3H, s, 18-CH_3), 0.83—0.92 (18H, m, 21-CH_3, 26-CH_3, 27-CH_3, Si-*tert*-Bu), 0.96 (3H, s, 19-CH_3), 3.57 (2H, m, 28-CH_2), 4.40 (1H, m, 3-H), 6.18—6.38 (2H, ABq, J=8.3 Hz, 6-H, 7-H), 7.40 (5H, m, C_6H_5).

(22*E*)-3′,5′-Dioxo-4′-phenyl-3β-(*tert*-butyldimethylsilyloxy)-5α,8α-[1′,2′]-1′,2′,4′-triazolidino-6,22-ergostadien-28-ol (12) C-20 aldehyde (**10**) (6.1 g, 10 mmol) was treated in a similar manner as described for **9** to give **12** (3.9 g, 56%) as an amorphous solid. ^{1}H-NMR ($CDCl_3$) δ: 0.08, 0.10 (each 3H, s, Si-CH_3), 0.81—0.88 (18H, m, 18-CH_3, 26-CH_3, 27-CH_3, Si-*tert*-Bu), 0.91 (3H, d, J=6.4 Hz, 21-CH_3), 0.96 (3H, s, 19-CH_3), 3.37—3.60 (2H, m, 28-CH_2), 4.41 (1H, m, 3-H), 5.15, 5.40 (each 1H, m, 22-H, 23-H), 6.17—6.38 (2H, ABq, J=8.3 Hz, 6-H, 7-H), 7.30—7.41 (5H, m, C_6H_5).

28-Iodo-3′,5′-dioxo-4′-phenyl-3β-(*tert*-butyldimethylsilyloxy)-5α,8α-[1′,2′]-1′,2′,4′-triazolidino-6-ergostene (13) A pyridine solution (20 ml) of **11** (4.2 g, 6 mmol) and *p*-toluenesulfonyl chloride (2.3 g, 6 mmol) was stirred at room temperature overnight. The mixture was extracted with ethyl acetate and washed with saturated $NaHCO_3$ solution and brine. After the solution was dried and concentrated, the residue was dissolved in acetone (50 ml). To this solution, NaI (5.0 g, 38 mmol) was added. After heating to reflux for 3 h, the mixture was extracted with chloroform, washed with 5% $Na_2S_2O_3$ solution and brine, dried and concentrated. Hexane was added to the residue to give **13** (4.2 g, 86%) as crystals. (mp 195—197 °C). ^{1}H-NMR ($CDCl_3$) δ: 0.08, 0.10 (each 3H, s, Si-CH_3), 0.80 (3H, s, 18-CH_3), 0.82—0.92 (18H, m, 21-CH_3, 26-CH_3, 27-CH_3, Si-*tert*-Bu), 0.97 (3H, s, 19-CH_3),

3.28 (2H, m, 28-CH_2), 4.40 (1H, m, 3-H), 6.18—6.37 (2H, ABq, J=8.3 Hz, 6-H, 7-H), 7.41 (5H, m, C_6H_5).

(22*E*)-28-Iodo-3′,5′-dioxo-4′-phenyl-3β-(*tert*-butyldimethylsilyloxy)-5α,8α[1′,2′]-1′,2′,4′-triazolidino-6,22-ergostadiene (14) Compound **12** (3.7 g, 5 mmol) was treated as described for **11** to give **14** (1.6 g, 40%) as an amorphous solid.

^{1}H-NMR ($CDCl_3$) δ: 0.08, 0.10 (each 3H, Si-CH_3), 0.81—0.89 (18H, m, 18-CH_3, 26-CH_3, 27-CH_3, Si-*tert*-Bu), 0.92 (3H, d, J=6.4 Hz, 21-CH_3), 0.96 (3H, s, 19-CH_3), 3.15, 3.24 (each 1H, m, 28-CH_2), 4.41 (1H, m, 3-H), 5.10, 5.33 (each 1H, m, 22-H, 23-H), 6.18—6.38 (2H, ABq, J=8.3 Hz, 6-H, 7-H), 7.41 (5H, m, C_6H_5).

Ergosta-5,7,24(28)-trien-3β-ol (17) A xylene solution (15 ml) of **13** (1.6 g, 2 mmol) and DBU (0.8 g, 4 mmol) was refluxed for 30 min. The solution was washed with brine and concentrated. The residue was purified by silica gel chromatography (chloroform–hexane, 4 : 1, v/v) to give **15** (610 mg, 61%) as a solid. A THF solution (10 ml) of **15** (610 mg, 1.2 mmol) and 1 M n-Bu_4NF (3 ml) was stirred at room temperature for 2 h. The solution was extracted with ethyl acetate, washed with brine and concentrated. The residue was purified by silica gel chromatography (chloroform) to afford **17** (410 mg, 86%) as crystals, mp 129—131 °C (MeOH) (lit.[9] 128—132 °C), $[\alpha]_D^{22}$ −100.0° (c=0.15, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.63 (3H, s, 18-CH_3), 0.95 (3H, s, 19-CH_3), 0.92—1.04 (9H, m, 21-CH_3, 26-CH_3, 27-CH_3), 3.66 (1H, m, 3-H), 4.66, 4.72 (each 1H, s, 28-CH_2), 5.39, 5.58 (each 1H, m, 6-H, 7-H).

A pyridine solution of **17** (100 mg) and acetic anhydride (0.5 ml) was heated at 80—85 °C with stirring for 1 h. The solution was extracted with ethyl acetate, washed with saturated $NaHCO_3$ and brine, and concentrated. The residue was purified by silica gel chromatography. Elution with chloroform gave the 3β-acetate of **17** (70 mg, 68%) as crystals. mp 133—135 °C (MeOH) (lit.[10b] 128—132 °C), $[\alpha]_D^{22}$ −79.8° (c=0.22, $CHCl_3$) (lit.[10b] −75.5°C (c=0.17, $CHCl_3$)).

Ergosta-5,7,22,24(28)-tetraen-3β-ol (18) Compound **14** (800 mg, 1 mmol) was treated as described for **13** to give **18** (236 mg, 60% from **14**) as crystals, mp 116—118 °C (EtOH) (lit.[10b] 118—120 °C), $[\alpha]_D^{22}$ −101.5° (c=0.1, $CHCl_3$) (lit.[22] −78° (c=1.0, $CHCl_3$)). ^{1}H-NMR ($CDCl_3$) δ: 0.65 (3H, s, 18-CH_3), 0.95 (3H, s, 19-CH_3), 1.06—1.10 (9H, m, 21-CH_3, 26-CH_3, 27-CH_3), 3.67 (1H, m, 3-H), 4.83, 4.86 (each 1H, s, 28-CH_2), 5.38, 5.95 (each 1H, m, 6-H, 7-H), 5.60, 5.95 (2H, ABq, J=5.6 Hz, 22-H, 23-H).

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