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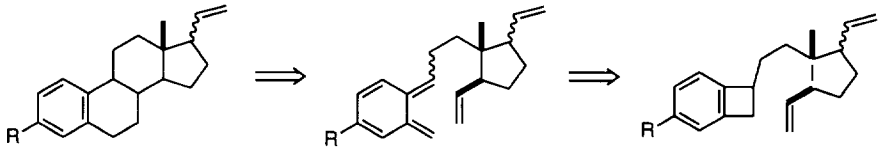
Dialkylation of 2,3-Butanedione Diketal with 1,8-Bis(trimethylsilyl)-2,6-octadiene (BISTRO). Application to the Synthesis of Estrone Derivatives

Hélène Pellissier and Maurice Santelli

Lab. de Synthèse Organique, URA au CNRS n°1411, Faculté de St-Jérôme, 13397 Marseille (France)
Fax: (33) 91 98 38 65; e-mail : m.santelli@lso.u-3mrs.fr

Abstract:Titanium tetrachloride mediated-dialkylation of 2,3-butanedione ketal **2** by 1,8-bis(trimethylsilyl)-2,6-octadiene (BISTRO) **1** led to 1-acetyl-1-methyl-2,5-divinylcyclopentane **4**. This latter was methoxycarbonylated (NaH/dimethylcarbonate) and then alkylated with iodobenzocyclobutene (Cs_2CO_3/acetone) to give a benzocyclobutenic intermediate **6**, whose thermolysis provided the 12-oxo-estrane derivatives **8** - **11**. Copyright © 1996 Elsevier Science Ltd

Important progress in steroid synthesis comes from the strategy involving an intramolecular Diels-Alder cycloaddition of *o*-quinodimethanes which are mostly generated by thermal ring opening of benzocyclobutenes.[1-4] This methodology has a remarkable advantage for the formation of the B/C cycle starting from an *o*-quinodimethane precursor and a cyclopentane derivative bearing a vinyl group.



In connection with our interest in steroid synthesis, we have recently reported a new strategy for the preparation of 1,1-disubstituted-2,5-divinylcyclopentanes. These latter arise from addition of 1,8-bis(trimethylsilyl)-2,6-octadiene **1** to different electrophilic reagents.[5,6]

We firstly used 1-methyl-1-(2-nitroethyl)-2,5-divinylcyclopentane, generated by treatment of 4-nitro-2-butanone ethylene ketal with BISTRO, as precursor of 17-vinyl-1,3,5(10)-estratrien-11-ones.[7]

In a second time, a γ-spirolactone, diastereoselectively elaborated by reaction of BISTRO with succinic anhydride[6] (or 3-carbomethoxypropionylchloride), was involved in a very short synthesis of 17-vinyl-1,3,5(10)-estratriene derivatives.[8]

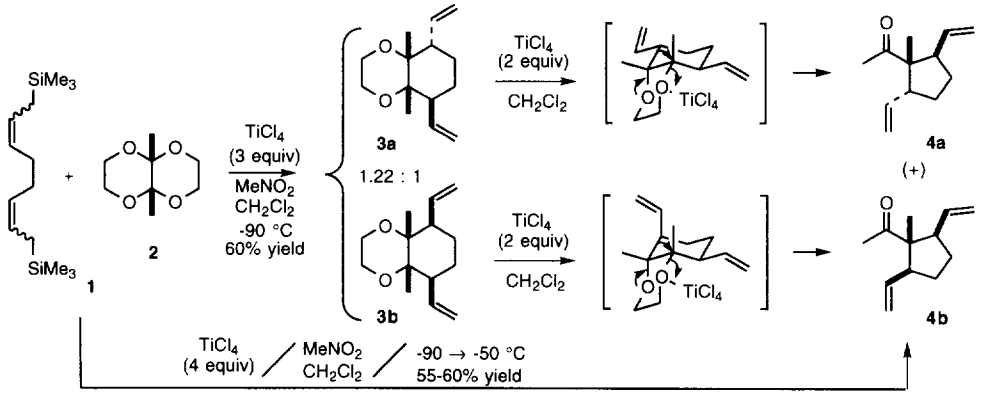
This paper reports a third and new approach to angularly substituted steroids based on the use of 1-acetyl-1-methyl-2,5-divinylcyclopentanes **4** as building blocks, whose synthesis was previously described.[9]

Effectively, we recently showed that addition of BISTRO with α-diketone diketal **2** (*cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane) carried out in the presence of three equivalents of titanium tetrachloride leads to *cis*-1,6-dimethyl-7,10-divinyl-2,5-dioxabicyclo[4.4.0]decanes **3a** and **3b**, with high diastereoselectivity, involving an invertive ("S_N2-like") substitution.

Compounds **3a** and **3b** are separated by chromatography and further converted quantitatively and stereospecifically into corresponding (*d,l*)- and (*meso*)-1-acetyl-1-methyl-2,5-divinylcyclopentanes **4a** and **4b** by treatment with $TiCl_4$, through a pinacol-like rearrangement.

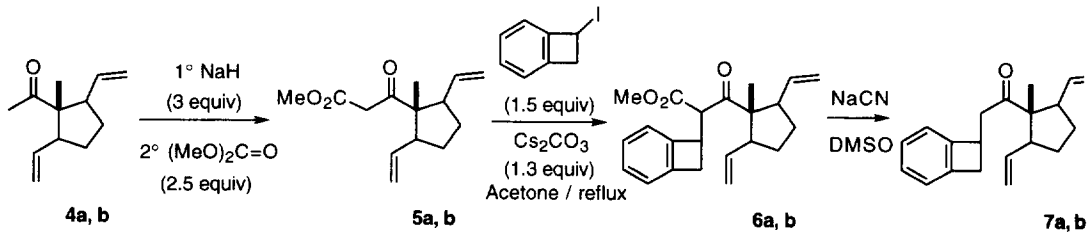
It is worth noting that, if the reaction of BISTRO with **2** is performed with four equivalents of $TiCl_4$ (instead of three equivalents for the synthesis of **3**) combined with a final reaction temperature increased up to -50°C, the expected ketones **4a** and **4b** are directly obtained in a similar yield (60% yield, **4a**:**4b** = 55:45).

However, it is useful to remark that chromatographic separation of ketones **4a** and **4b** is more difficult than that of dioxanes **3a** and **3b**.

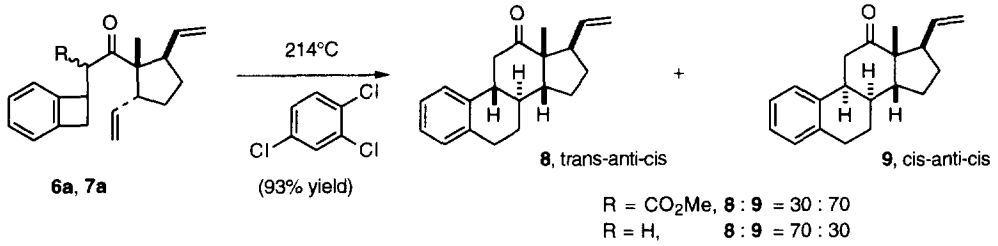


Each ketone **4a** or **4b** is then carbomethoxylated by treatment with sodium hydride and dimethylcarbonate to give the corresponding β-keto-ester **5a** or **5b** in 71% yield.

The next step is the alkylation of **5a** or **5b** with iodobenzocyclobutene[10] in the presence of Cs_2CO_3, which leads to the benzocyclobutenic intermediates **6a** or **6b**, respectively, in 95% yield (mixture of isomers).



Thermolysis of compound exhibiting the (*d,l*) configuration, **6a** or **7a** (arising from **6a** by a Krapcho process[11]), affords a mixture of 17-vinyl-12-oxoestrane derivatives **8** and **9** in 93% yield.

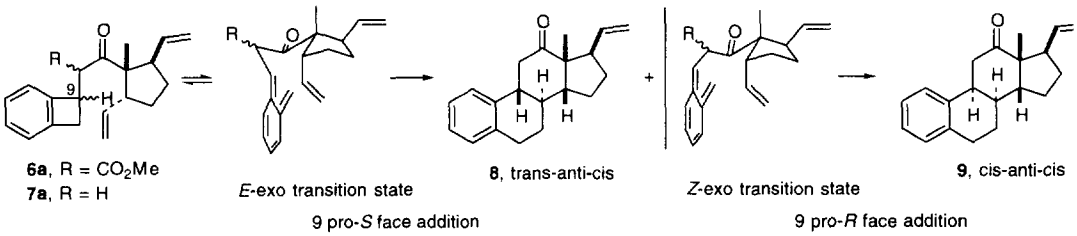


The proportions of the two isomers are markedly different according to the nature of the precursor **6a** or **7a**.

Thus, upon heating, compound **6a** gives, after an *in situ* decarbomethoxylation[12], a **8**:**9** ratio of 30:70. In contrast, the **8**:**9** ratio is reversed (70:30) in the case of the thermolysis of **7a**.

We assume that only the vinyl group *syn* to the benzocyclobutene moiety is involved in the cycloaddition process of **6a** or **7a** (100% stereoselectivity). Obviously, the other vinyl group is totally unreactive.

The diastereoisomeric mixture could result from an *exo* approach of either the *E o*-xylylene (for compound **8**) or the *Z o*-xylylene (for compound **9**) during the Diels-Alder process.



Effectively, an *endo* approach seems impossible according to inspection of molecular models.

The torquoselectivity in the electrocyclic conversion of benzocyclobutenes into *o*-xylylenes has been previously discussed.[13]

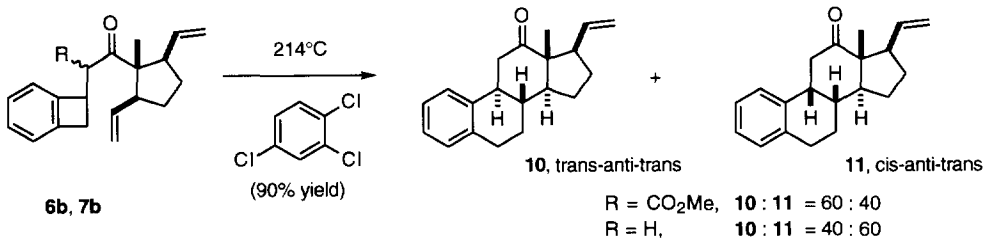
Generally, a prononced preference for outward rotation (*E o*-xylylene formation) is observed in the case of electron-donating substituents beared by the benzocyclobutene.

While, a net preference for inward rotation of electron-withdrawing groups is usually accepted.

However, several papers have reported towards the synthesis of polycyclic compounds, which can result exclusively from an inward rotation (Z *o*-xylylene) combined with an *exo* transition state.[3a,14]

Thermolysis of the *meso* precursor **6b** or **7b** leads in 90% yield to a mixture of steroids **10** and **11** in comparative proportions.

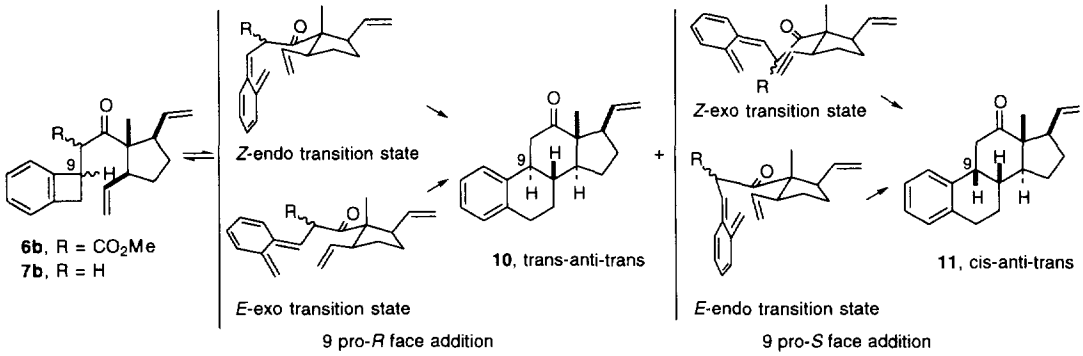
Compound **10** possesses the *trans-anti-trans* fused skeleton of natural steroids, while isomer **11** exhibits a *cis* B/C ring junction combined with a *trans* C/D ring junction.



Inspection of molecular models of **6b** (or **7b**) reveals that, in this case, an *endo* approach is possible.

Thus, the *trans* B/C ring junction of **10** could arise from either an *endo* approach of the *Z o*-xylylene or an *exo* approach of the *E o*-xylylene.

Similarly, an *exo* transition state involving the Z *o*-xylylene or an *endo* transition state of the E *o*-xylylene can explain the formation of **11**, as depicted below:



More generally, the following scheme summarizes the expected stereochemistry of the created B/C ring junction according to the nature of the rotation of the benzocyclobutene substituents (inward or outward) and the nature of the approach (*exo* or *endo*) :

o-xylylene	transition state	stereochemistry of the B/C ring junction
E (outward opening)	*endo*	*cis*
E (outward opening)	*exo*	*trans*
Z (inward opening)	*endo*	*trans*
Z (inward opening)	*exo*	*cis*

On the other hand, the stereochemistry of the C/D ring junction is controlled by the relative position of the vinyl group which is involved in the cycloaddition.

Conclusion : This new procedure constitutes a novel and convenient route to estrone derivatives through a five-step sequence from 1,3-butadiene. Application of this process to other α-diketone diketals is under progress, in order to prepare variously substituted estrane derivatives and among them, optically active relatives.

EXPERIMENTAL SECTION

General. All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F_{254}. ^1H and ^{13}C NMR spectra were recorded at 200 or 400 and 50 or 100 MHz respectively. Carbon-proton couplings were determined by DEPT sequence experiments. The structures of the steroids were more precisely established by a series of 1D, NOESY, NOE and decoupling experiments. The ^1H NMR coupling constants were determined on 1D-COSY spectra with semiselective excitation unit on a 400 MHz spectrometer.[15] Diastereoselectivity was determined by GC (for compounds **3** and **4**) or ^1H NMR analyses prior to any purification. Dichloromethane was distilled from P_2O_5 and tetrahydrofuran (THF) over sodium/benzophenone.

• **1,8-Bis(trimethylsilyl)-2,6-octadiene (BISTRO) 1** is prepared according to the previously described procedure.[16]

• ***Cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane 2** is quantitatively prepared by acetalisation of butane-2,3-dione (biacetyl) with ethane-1,2-diol as a single product.[17]

• **Iodobenzocyclobutene** is generated through a six-step sequence.
Anthranilic acid is easily converted into benzocyclobutenone, according to literature procedure[10]. This latter is quantitatively reduced by $LiAlH_4$ in THF. The alcohol is then transformed into the corresponding mesylate ($ClSO_2Me$, NEt_3, CH_2Cl_2). The crude mixture is directly treated by NaI (in refluxed acetone) to give expected iodobenzocyclobutene. The overall yield of the sequence is 29% (calculated from anthranilic acid).

• **Preparation of dioxadecaline derivatives 3a and 3b.**

A three-necked flask equipped with a thermometer, septum cap, magnetic stirring bar, and argon outlet is charged with anhydrous CH_2Cl_2 (10 mL) and anhydrous nitromethane (0.45 mL, 8.3 mmol). The solution is cooled at -80°C and $TiCl_4$ is added (0.7 mL, 6.3 mmol) and then 2,3-butanedione ketal **2** (0.348 g, 2 mmol) in CH_2Cl_2 (2 mL). After 20 min of stirring at -80°C, the solution is cooled at -90°C and BISTRO (1.020 g, 4 mmol) in CH_2Cl_2 (2 mL) is added over 10 min and stirred for 1h. The reaction is quenched by addition of aqueous saturated NH_4Cl solution (20 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The extracts are washed until neutrality, dried over $MgSO_4$ and concentrated under vacuum. The residue is purified by chromatography on silica gel eluting with a gradient of pentane-diethylether. Compound **3a** is first isolated (146 mg, 33% yield) and then compound **3b** (120 mg, 27% yield).

• **Direct obtention of ketones 4a and 4b.**

A similar procedure as before is employed, but using four equivalents of $TiCl_4$, combined with a higher temperature at the end of the reaction (one hour at -90°C and then twelve hours at -50°C). Similar yield and ratio **4a**:**4b** are obtained as for the synthesis of dioxanes **3a** and **3b** (60% yield, **4a**:**4b** = 55:45). Ketones **4a** and **4b** are more difficult to separate by chromatography than the corresponding dioxanes. The best compromise is to methoxycarboxylate the mixture of ketones **4a** and **4b**. The β-keto-esters **5a** and **5b** are then readily separated by chromatography.

• **Pinacol-rearrangement of 3 into 4.**

$TiCl_4$ (0.24 mL, 2 mmol) is added under argon, at -50°C to a solution of the dioxane **3** (0.222 g, 1 mmol) in CH_2Cl_2 (5 mL). The mixture is stirred for twelve hours at -50°C and then poured in an aqueous saturated

NH_4Cl solution (15 mL) and extracted with CH_2Cl_2. The extracts are successively washed, dried over $MgSO_4$ and concentrated under vacuum. The residue is purified by chromatography on silica gel (pentane-diethylether) to give the ketone **4** in 95% yield (0.169 g).

• Carbomethoxylation of 4 into β-keto-ester 5.

A 55% solution of NaH in oil (0.143 g, 3 mmol), 5 mL of dry THF and 0.21 mL (2.5 mmol) of dimethylcarbonate are mixed and then brought to reflux under argon. The ketone **4** (0.178 g, 1 mmol) is added and then stirred at reflux for 24 hours. After cooling to room temperature, 0.3 mL of acetic acid is added and then 5 mL of water. The mixture is extracted with diethylether. The organic layer is washed with water, dried over $MgSO_4$ and then concentrated under vacuum. The residue is chromatographied on silica gel, eluting with a gradient of pentane-diethylether. Compound **5b** is first isolated (92 mg, 39%) and then compound **5a** (76 mg, 32%).

• Synthesis of benzocyclobutenic derivative 6.

The β-keto-ester **5** (236 mg, 1 mmol) is dissolved in 5 mL of acetone. Cs_2CO_3 (489 mg, 1.5 mmol) and iodobenzocyclobutene (345 mg, 1.5 mmol) are successively added. The mixture is brought to reflux under argon for 24 hours. The reaction is cooled to room temperature, filtered and then evaporated under vacuum. The residue is chromatographied on silica gel (pentane/diethylether) to give the expected compound **6** as a mixture of several isomers.

• Krapcho decarboxylation of 6 into 7.

A mixture of **6** (338 mg, 1 mmol), 3 mL of DMSO and NaCN (148 mg, 3 mmol) is heated at 90°C under argon for 22 hours. After cooling at room temperature, the mixture is poured in 15 mL of water and then extracted with CH_2Cl_2. The organic layer is washed with water, filtered and concentrated under vacuum. The residue is chromatographied on silica gel, eluting with a gradient of pentane-diethylether. Compound **7** is isolated in 70% yield (196 mg) as a mixture of isomers.

• General procedure for the thermolysis of precursor 6 or 7 into estrone derivatives 8-11.

The benzocyclobutenic precursor **6** or **7** (1 mmol) is dissolved in 10 mL of 1,2,4-trichlorobenzene and boiled under argon for 22 hours. The mixture is then concentrated under vacuum. The residue is chromatographied on silica gel (eluting by pentane/diethylether). In each case of precursor, two methoxydecarboxylated diastereoisomers are isolated in 90-93% total yield.

Precursor (*d,l*) **6a** leads to a mixture of steroids **8** (Mp 70 °C) and **9** (oil) (252 mg, 90%, **8:9** = 30:70) which can be separated by crystallisation in pentane.

An inversed ratio is obtained (**8:9** = 70:30) in the case of precursor (*d,l*) **7a**.

Precursor *meso* **6b** gives 104 mg (37%) of **10** (Mp 102 °C), which is the first eluted during the chromatography and 156 mg (56%) of **11** (Mp 54 °C).

Precursor *meso* **7b** provides 156 mg (56%) of **10**, along with 104 mg (37%) of **11**.

Spectroscopic data of steroids 8-11

• 8α,9β,14β,17β-vinyl-1,3,5(10)-estratrien-12-one 8.

IR (nujol) 3080, 1710, 915, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17-7.12 (4H, m), 5.75 (1H, ddd, *J* = 17.3, 10.4, 7.0 Hz, H20), 5.03 (1H, ddd, *J* = 10.4, 1.8, 1.2 Hz, H21), 4.96 (1H, dt, *J* = 17.3, 1.8 Hz, H21), 3.12 (1H, dd, *J* = 15.6, 4.7 Hz, H11), 2.90 (4H, m), 2.48 (1H, dd, *J* = 15.6, 12.9 Hz, H11), 2.10 (2H, m), 1.94 (1H, dq, *J* = 12.3, 8.06 Hz), 1.82 (1H, ddd, *J* = 11.2, 4.1, 3.6 Hz, H14), 1.66 (2H, m), 1.45 (1H, qd, *J* = 11.2, 2.35 Hz, H8), 1.34 (1H, tt, *J* = 11.3, 8.77 Hz), 1.05 (3H, s, H18); ^{13}C NMR ($CDCl_3$) δ 212.0 (s), 138.4 (s), 137.6 (d) (C20), 136.7 (s), 129.2 (d), 126.2 (d) (2C), 126.1 (d), 115.9 (t) (C21), 57.9 (d) (C14), 55.8 (s) (C13), 49.3 (d) (C17), 43.7 (t) (C11), 42.9 (d) (C8), 41.5 (d) (C9), 30.0 (t) (C6), 28.7 (t), 28.0 (t) (2C), 19.0 (q) (C18). Anal. calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.49; H, 8.52.

• 8α,9α,14β,17β-vinyl-1,3,5(10)-estratrien-12-one 9.

IR (neat) 3080, 2950, 2885, 1705, 1640, 1460, 1380, 915, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (4H, br s), 5.73 (1H, m), 5.03 (2H, m), 3.41 (1H, ddd, *J* = 9.0, 6.3, 4.4 Hz, H9), 3.03 (1H, q, *J* = 8.0 Hz, H17), 2.87-2.80 (2H, m), 2.76 (1H, dd, *J* = 15.9, 9.0 Hz, H11), 2.70 (1H, dd, *J* = 15.9, 6.3 Hz, H11), 2.09 (2H, m), 2.0-1.8 (2H, m), 1.8-1.6 (2H,m), 1.6-1.52 (2H,m), 0.97 (3H,s); ^{13}C NMR ($CDCl_3$) δ 215.0 (d), 139.1 (s), 138.2 (d), 136.0 (s), 129.1 (d), 128.0 (d), 126.3 (d), 126.1 (d), 115.6 (t), 56.2 (s) (C13), 52.4 (d) (C14), 50.0 (d) (C17), 42.5 (t) (C11), 37.9 (d) (C9), 37.4 (d) (C8), 30.2 (t), 28.9 (t), 28.6 (t), 25.7 (t), 20.9 (q). MS (EI) *m/z* 280 (31), 262 (18), 247 (11), 237 (23), 236 (31), 144 (38), 129 (50), 108 (100), 93 (31), 91 (40), 79 (30), 43 (20), 41 (23); HRMS calcd for $C_{20}H_{24}O$ 280.1811, found 280.1827.

• 8β,9α,14α,17β-vinyl-1,3,5(10)-estratrien-12-one 10.

IR (neat) 3080, 2950, 2885, 1700, 1640, 1460, 1380, 915, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (4H, br s), 6.00 (1H, ddd, *J* = 17.4, 10.6, 6.0 Hz), 5.12 (1H, dt, *J* = 17.4, 1.85 Hz), 5.09 (1H, dt, *J* = 10.6, 1.8 Hz, H21), 2.97 (2H,m), 2.93 (1H, dd, *J* = 12.0, 3.6 Hz, H11), 2.84 (1H, br dd, *J* = 9.2, 6.0 Hz, H17), 2.73 (1H, m, H14), 2.68 (1H, dd, *J* = 12.8, 12.0 Hz, H11), 2.02 (1H, dtd, *J* = 12.7, 5.9, 2.9 Hz, H7), 1.9 (2H,m),1.86 (1H, qd, *J* = 11.5, 2.9 Hz, H8), 1.7 (1H,m), 1.65 (1H, td, *J* = 11.5, 6.9 Hz, H9), 1.55-1.40 (2H, m), 0.94 (3H,s); ^{13}C NMR ($CDCl_3$) δ 213.5 (s), 139.0 (s), 138.9 (d) (C20), 136.5 (s), 129.2 (d), 126.4 (d), 126.1 (d), 125.0 (d), 115.3 (t) (C21), 56.8 (s) (C13), 54.9 (d) (C9), 46.5 (d) (C17), 46.0 (d) (C14), 42.6 (t) (C11), 38.0 (d) (C8), 29.5 (t) (C6), 27.4 (t) (C7), 24.9 (t) (C15), 23.7 (t) (C16), 13.1 (q) (C18). Anal. calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.76; H, 8.57.

• 8β,9β,14α,17β-vinyl-1,3,5(10)-estratrien-12-one 11.

IR (neat) 3080, 2950, 2885, 1705, 1640, 1460, 1380, 915, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (1H, d, *J* = 7.7 Hz), 7.14 (1H, t, *J* = 7.2 HZ), 7.09 (1H, t, *J* = 7.3 Hz), 7.05 (1H, d, *J* = 7.3 Hz), 6.01 (1H, m), 5.02 (2H, m), 3.48 (1H, q, *J* = 6.0 Hz), 2.91 (1H, dd, *J* = 15.5, 6.1 Hz, H11), 2.83 (1H, dd, *J* = 15.5, 5.8 Hz, H11), 2.76 (1H, ddd, *J* = 16.2, 9.1, 5.9 Hz), 2.66 (1H, dd, *J* = 16.2, 5.9 Hz), 2.56 (1H, br q, *J* = 6.2 Hz), 2.37 (1H, sext, *J* = 5.7 Hz), 1.97 (1H, qt, *J* = 9.2, 5.1 Hz), 1.70 (4H, m), 1.47 (1H, dd, *J* = 11.5, 6.2 Hz), 1.43 (1H, dd, *J* = 11.5, 5.8 Hz), 1.02 (3H, s); ^{13}C NMR ($CDCl_3$) δ 214.0 (s), 139.0 (d), 137.4 (s), 137.3 (s), 128.6 (d), 127.3 (d), 126.2 (d), 125.9 (d), 115.0 (t), 55.2 (s), 48.8 (d), 46.5 (d), 42.0 (t), 39.4 (d), 33.8 (d), 26.8 (t), 25.5 (t), 24.6 (t), 23.9 (t), 13.0 (q). Anal. calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.82; H, 8.54.

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