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Regiochemistry of Wacker-Type Oxidation of Vinyl Group in the Presence of Neighboring Oxygen Functions. Part 1.

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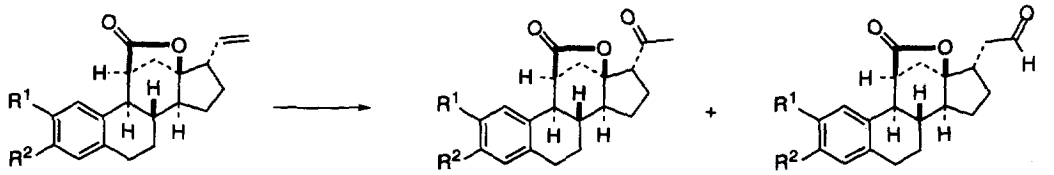
Palladium(II) oxidation of (±)-17α-vinyl-1,3,5(10)-gonatriene derivatives **1** bearing a lactonic bridge on the β-face affords the expected acetyl derivatives. In contrast, when the lactonic bridge or a hydroxy group is present on the α-face (syn relationship), aldehydes resulting from an anti-Markovnikov hydroxypalladation are obtained in appreciable yields. © 1997 Elsevier Science Ltd.

The palladium(II) oxidation of terminal olefins to give methyl ketones (Wacker process) is well established both as an industrial and a synthetic organic reaction.[1] This reaction appears to involve Markovnikov hydroxypalladation followed by palladium hydride elimination to give methyl ketones and Pd(0).[2] Thus, terminal olefins can be regarded as masked methyl ketones.

In a previous paper, we reported a five step synthesis of (±)-17-vinyl-1,3,5(10)-gonatriene derivatives from 1,3-butadiene.[3,4] As an extension of this work, we considered the possibility of unmasking the vinyl group by catalytic oxidation.[5] Palladium catalyzed oxidation gave unsatisfactory results when cuprous chloride and oxygen were used as co-reagents.[6] Fortunately, palladium acetate-benzoquinone oxidation, performed in the presence of perchloric acid,[7] provided a convenient route to oxidized compounds [$Pd(OAc)_2$, 10%; benzoquinone; $HClO_4$ (0.3 M); acetonitrile].

As expected, treatment of (±)-17α-vinyl-1,3,5(10)-gonatriene derivatives **1**, bearing a lactonic bridge on the β-face, afforded the (±)-17α-acetyl-1,3,5(10)-gonatriene derivatives **2** in good yields. However, minor amounts of the unexpected terminal aldehydes **3** were obtained besides ketones **2**.



1a: $R^1 = R^2 = H$
1b: $R^1 = OMe$, $R^2 = H$
1c: $R^1 = R^2 = OMe$

2a: $R^1 = R^2 = H$, 85%
2b: $R^1 = OMe$, $R^2 = H$, 79%
2c: $R^1 = R^2 = OMe$, 77%

3a: $R^1 = R^2 = H$, 7%
3b: $R^1 = OMe$, $R^2 = H$, 14%
3c: $R^1 = R^2 = OMe$, 9%

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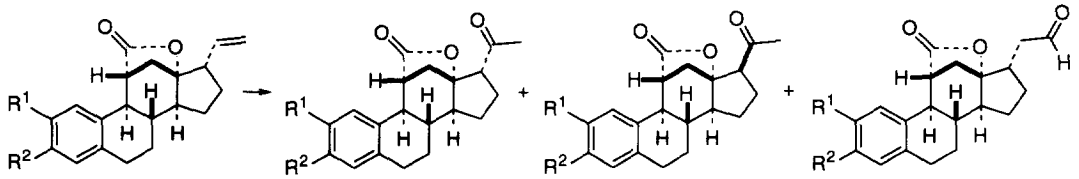
In marked contrast, oxidation of the isomeric (±)-17α-vinyl-1,3,5(10)-gonatriene derivatives **4**, bearing a lactonic bridge on the α-face, afforded a mixture of methyl ketone derivatives (expected α-acetyl compounds **5** and epimerized β-acetyl compounds **6**) and aldehydes **7**.



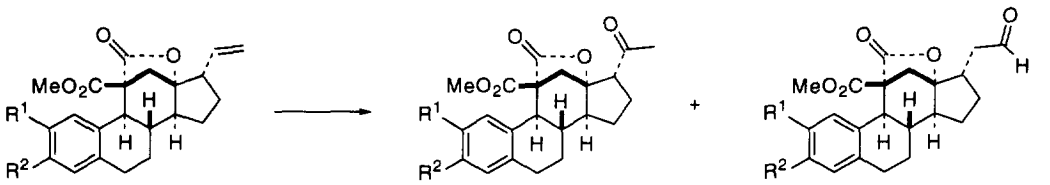
4a: $R^1 = R^2 = H$
4b: R^1 = OMe, $R^2 = H$
4c: $R^1 = R^2$ = OMe

5a: $R^1 = R^2 = H$, 35%
5b: R^1 = OMe, $R^2 = H$, 35%
5c: $R^1 = R^2$ = OMe, 35%

6a: $R^1 = R^2 = H$, 10%
6b: R^1 = OMe, $R^2 = H$, 8%
6c: $R^1 = R^2$ = OMe, 10%

7a: $R^1 = R^2 = H$, 35%
7b: R^1 = OMe, $R^2 = H$, 28%
7c: $R^1 = R^2$ = OMe, 30%

Moreover, aldehydes **10** are major products from (±)-11β-carbomethoxy-17α-vinyl-1,3,5(10)-gonatriene derivatives **8** which exhibit a lactonic bridge on the α-face.

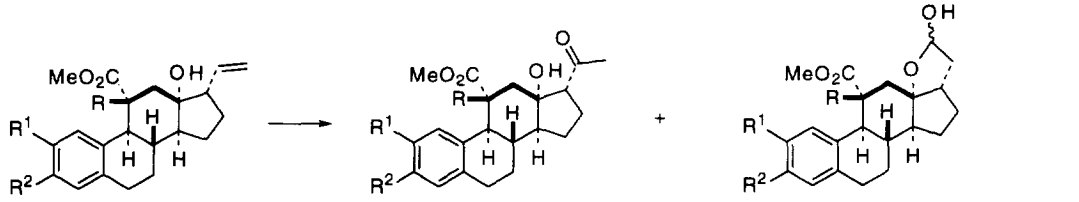


8a: $R^1 = R^2 = H$
8b: R^1 = OMe, $R^2 = H$
8c: $R^1 = R^2$ = OMe

9a: $R^1 = R^2 = H$, 0%
9b: R^1 = OMe, $R^2 = H$, 38%
9c: $R^1 = R^2$ = OMe, 24%

10a: $R^1 = R^2 = H$, 37%
10b: R^1 = OMe, $R^2 = H$, 45%
10c: $R^1 = R^2$ = OMe, 28.5%

Similarly, lactols **13** or **16** were obtained, respectively, from the (±)-11α-carbomethoxy-13α-hydroxy-17α-vinyl-1,3,5(10)-gonatriene derivatives **11** or **14** along with the acetyl compounds **12** or **15**.

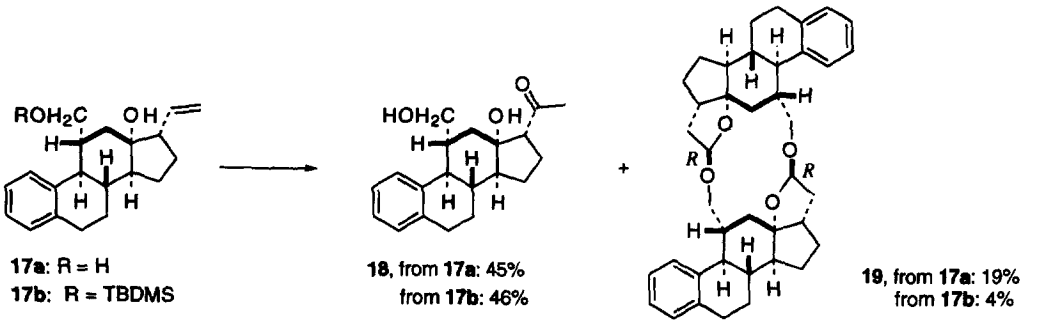


11a: R = $R^1 = R^2 = H$
11b: R^1 = OMe, R = $R^2 = H$
11c: R = H, $R^1 = R^2$ = OMe
14: R = CO_2Me, $R^1 = R^2 = H$

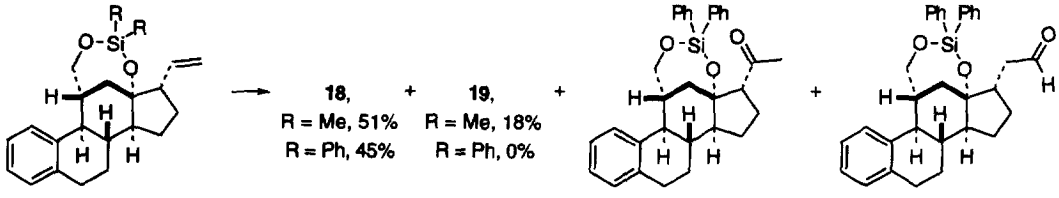
12a: R = $R^1 = R^2 = H$, 46%
12b: R^1 = OMe, R = $R^2 = H$, 58%
12c: R = H, $R^1 = R^2$ = OMe, 54%
15: R = CO_2Me, $R^1 = R^2 = H$, 46%

13a: R = $R^1 = R^2 = H$, 37%
13b: R^1 = OMe, R = $R^2 = H$, 22%
13c: R = H, $R^1 = R^2$ = OMe, 22%
16: R = CO_2Me, $R^1 = R^2 = H$, 37%

The oxidation of the 13α-hydroxy derivatives **17** afforded β-ketodiols **18** and bis-ketal **19**. The stereostructure of the bis-ketal **19** was assigned on the basis of its MS (*m/z* = 592) and NMR studies (COSY and selective COSY). The C_{2v} structure was confirmed by the presence of only 22 signals in ^{13}C NMR spectra. The formation of this ketal was under thermodynamical control.[8] We have checked that **19** was the more stable bis-ketal by semi-empirical calculations with PM3 method.[9] Calculations revealed that **19** ($\Delta H_f = -119.78$ kcal.mol^{-1}) was more stable than the alternative structure with a *S, S* configuration ($\Delta H_f = -93.91$ kcal.mol^{-1}).



Afterwards, the diol **17a** was converted into **20** by protection of the diol function. This latter was then submitted to the Wacker oxidation. A mixture of corresponding ketones **21** and or aldehyde derivatives **22** was isolated, along with ketal **19** and diol **18** arising from hydrolysis of the protecting group.

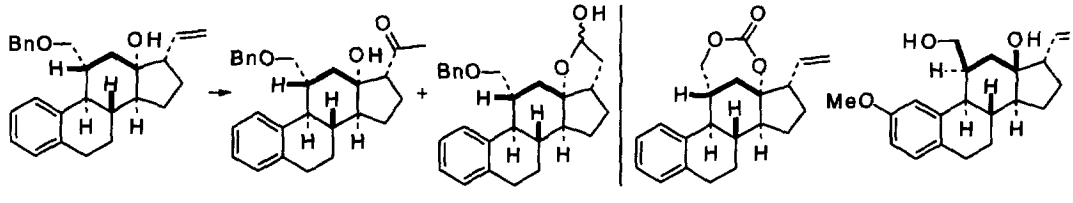


20a: R = Me
20b: R = Ph

21, 7%

22, 11%

Alternatively, the protection of the hydroxymethyl group of the diol **17a** as a benzyl ether **23** gave rise to acetyl and aldehyde derivatives **24** and **25**.



23 **24**, 60% **25**, 39% **26** **27**

Finally, (±)-11α-hydroxymethyl-13α-hydroxy-17α-vinyl-1,3,5(10)-gonatriene derivative **26** was recovered unchanged even after 2 h under the same oxidative conditions. By the same way, the oxidation of **27** which exhibits two hydroxy groups in the β face, did not lead to any oxidized compounds.

The formation of aldehydes was explained by postulating that palladium coordinates to the oxygen atom borne by the function situated in the α-face. These results will be discussed in the following paper.

EXPERIMENTAL SECTION

General. 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. The preparation of 17-vinyl-1,3,5(10)-gonatriene derivatives is to be published.

General Procedure for the Wacker Process.

To a solution of 0.1 mmol of palladium acetate (22.4 mg, 0.1 equiv) and 0.5 mmol of benzoquinone (0.54 g, 0.5 equiv) in 10 mL of acetonitrile, 3.1 mL of water and 0.65 mL of perchloric acid (70 %) (0.16 mL for **23**) were successively added. The mixture was stirred 0.5 h at 20 °C under argon. Then a solution of the steroid derivative (1 mmol) in 12 mL of acetonitrile was added and stirred at 20 °C for 1.5 h. The mixture was poured in diethyl ether and washed with a solution of NaOH (30 %). The aqueous layer was extracted with ether. The combined organic layers were dried over magnesium sulfate, filtrated and concentrated under vacuum. The crude product was purified by chromatography on silica gel.

17α-Acetyl-11β,13β-carbolactonegona-1,3,5(10)-triene (2a). White solid: mp 153 °C; IR 1770, 1711, 1376, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.23 (m, 4H), 3.50 (dd, J = 5.5, 1.6 Hz, 1H), 3.39 (dd, J = 9.4, 5.2 Hz, 1H), 2.89 (m, 2H), 2.74 (d, J = 10.9 Hz, 1H), 2.51 (dd, J = 11.7, 5.5 Hz, 1H), 2.26 (m, 1H), 2.23 (s, 3H), 2.19 (d, J = 11.7 Hz, 1H), 2.03 (m, 2H), 1.92 (ddd, J = 11.8, 9.4, 7.4 Hz, 1H), 1.83 (dddd, J = 13.5, 9.4, 8.6, 5.2 Hz, 1H), 1.63 (m, 2H), 1.49 (dq, J = 11.8, 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 208.8 (s), 175.8 (s), 136.5 (s), 135.4 (s), 129.2 (d), 126.5 (d), 125.6 (d), 124.9 (d), 94.7 (s), 56.6 (d), 50.1 (d), 44.1 (d), 41.8 (d), 40.7 (d), 38.9 (t), 31.4 (q), 28.8 (t), 27.9 (t), 27.7 (t), 27.4 (t). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.45; H, 7.05.

11β,13β-Carbolactone-17α-(2-oxoethyl)gona-1,3,5(10)-triene (3a). White solid: mp 114 °C; IR 3052, 1771, 1725, 1380, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.77 (t, J = 2.1 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.15 (m, 3H), 3.53 (dd, J = 5.5, 1.5 Hz, 1H), 2.89 (m, 2H), 2.79 (tt, J = 9.8, 5.0 Hz, 1H), 2.71 (d, J = 10.0 Hz, 1H), 2.59 (ddd, J = 17.0, 5.2, 2.1 Hz, 1H), 2.49 (dd, J = 11.3, 5.5 Hz, 1H), 2.32 (ddd, J = 17.0, 9.8, 2.1 Hz, 1H), 2.31 (m, 1H), 2.01 (m, 2H), 1.84 (d, J = 11.3 Hz, 1H), 1.70 (m, 1H), 1.61 (m, 2H), 1.50 (m, 1H), 1.39 (dq, J = 8.6, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 200.5 (d), 175.7 (s), 136.5 (s), 135.3 (s), 129.3 (d), 126.5 (d), 125.7 (d), 124.9 (d), 96.0 (s), 49.3 (d), 46.3 (t), 44.3 (d), 42.2 (d), 40.9 (d), 38.3 (t), 38.3 (d), 30.4 (t), 28.9 (t), 27.5 (t), 27.0 (t). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.45; H, 7.06.

17α-Acetyl-11β,13β-carbolactone-2-methoxygona-1,3,5(10)-triene (2b). White solid: mp 132 °C; IR 1770, 1709, 1210, 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.93 (m, 2H), 6.64 (dd, J = 8.3, 2.3 Hz, 1H), 3.73 (s, 3H), 3.39 (d, J = 5.6 Hz, 1H), 3.34 (dd, J = 9.4, 5.1 Hz, 1H), 2.75 (m, 2H), 2.67 (d, J = 9.4 Hz, 1H), 2.46 (dd, J = 11.8, 5.6 Hz, 1H), 2.19 (s, 3H), 2.14 (d, J = 11.8 Hz, 1H), 1.87 (m, 5H), 1.50 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 208.9 (s), 175.5 (s), 157.4 (s), 136.5 (s), 129.8 (d), 128.3 (s), 111.7 (d), 111.1 (d), 94.5 (s), 56.5 (d), 55.0 (q), 49.5 (d), 44.1 (d), 41.9 (d), 40.6 (d), 38.8 (t), 31.2 (q), 27.9 (t), 27.8 (t), 27.5 (t), 27.4 (t). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.11; H, 7.06. Found: C, 74.20; H, 7.02.

11β,13β-Carbolactone-2-methoxy-17α-(2-oxoethyl)gona-1,3,5(10)-triene (3b). White solid: mp 124 °C; IR 3045, 1775, 1732, 1245 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.72 (s, 1H), 6.92 (m, 2H), 6.66 (d, J = 8.3 Hz, 1H), 3.73 (s, 3H), 3.41 (d, J = 5.7 Hz, 1H), 2.75 (m, 5H), 2.62 (m, 1H), 2.48 (dd, J = 11.3, 5.7 Hz, 1H), 2.28 (m, 2H), 1.98 (m, 2H), 1.80 (d, J = 11.3 Hz, 1H), 1.61 (m, 1H), 1.51 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 200.5 (d), 175.6 (s), 157.8 (s), 136.5 (s), 130.2 (d), 128.6 (s), 112.1 (d), 111.3 (d), 95.9 (s), 55.4 (q), 49.7 (d), 46.5 (t), 44.7 (d), 42.6 (d), 41.0 (d), 38.9 (t), 38.6 (d), 30.5 (t), 28.3 (t), 27.8 (t), 27.1 (t).

17α-Acetyl-11β,13β-carbolactone-2,3-dimethoxygona-1,3,5(10)-triene (2c). White solid: mp 170 °C (EtOAc); IR 1773, 1710, 1350, 1215, 1138, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.85 (s, 1H), 6.55 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.39 (m, 2H), 2.79 (m, 2H), 2.69 (d, J = 10.2 Hz, 1H), 2.49 (dd, J = 11.7, 5.5 Hz, 1H), 2.23 (m, 1H), 2.23 (s, 3H), 2.12 (d, J = 11.7 Hz, 1H), 1.92 (m, 4H), 1.53 (m, 3H); ^{13}C

NMR ($CDCl_3$) δ 208.5 (s), 175.5 (s), 147.3 (s), 146.5 (s), 128.5 (d), 127.2 (d), 111.9 (d), 108.6 (d), 94.5 (s), 56.4 (d), 55.8 (q), 55.5 (q), 49.7 (d), 43.7 (d), 42.3 (d), 40.9 (d), 38.8 (t), 31.2 (q), 28.7 (t), 28.0 (t)(2C), 27.8 (t); MS *m/z* 370 (100), 281 (3), 255 (3), 201 (8), 189 (15). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.03. Found: C, 71.25; H, 7.12.

11β,13β-Carbolactone-2,3-dimethoxy-17α-(2-oxoethyl)gona-1,3,5(10)-triene (3c). White solid: mp 145 °C; IR 1768, 1720, 1256, 1216 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.80 (s, 1H), 6.82 (s, 1H), 6.53 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.43 (d, *J* = 5.5 Hz, 1H), 2.77 (m, 3H), 2.65 (m, 2H), 2.49 (dd, *J* = 11.2, 5.5 Hz, 1H), 2.35 (dd, *J* = 11.7, 2.1 Hz, 1H), 1.94 (m, 2H), 1.83 (d, *J* = 11.2 Hz, 1H), 1.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 200.5 (d), 175.7 (s), 147.1 (s), 146.9 (s), 128.8 (s), 127.3 (s), 112.2 (d), 108.8 (d), 96.1 (s), 56.1 (q), 55.9 (q), 49.4 (d), 46.5 (t), 44.4 (d), 42.9 (d), 41.4 (d), 38.9 (t), 38.5 (d), 30.5 (t), 28.9 (t), 27.9 (t), 27.1 (t). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.03. Found: C, 71.25; H, 7.15.

17α-Acetyl-11α,13α-carbolactonegona-1,3,5(10)-triene (5a). White solid: mp 163 °C; IR 1774, 1760, 1376 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 7.21 (m, 4H), 3.15 (d, *J* = 4.8 Hz, 1H), 2.81 (m, 3H), 2.29 (dd, *J* = 10.5, 6.7 Hz, 1H), 2.11 (m, 1H), 2.05 (s, 3H), 1.85 (m, 1H), 1.78 (dd, *J* = 12.3, 4.8 Hz, 1H), 1.58 (d, *J* = 12.3 Hz, 1H), 1.51 (m, 3H), 1.12 (m, 2H), 0.55 (ddd, *J* = 17.5, 11.5, 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 204.6 (s), 179.2 (s), 137.9 (s), 136.6 (s), 129.2 (d), 126.3 (d), 125.7 (d), 124.1 (d), 93.0 (s), 58.1 (d), 51.5 (d), 40.9 (d), 40.4 (d), 39.9 (d), 33.8 (t), 30.5 (q), 29.0 (t), 28.7 (t), 27.0 (t), 26.6 (t). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.47; H, 7.08.

17β-Acetyl-11α,13α-carbolactonegona-1,3,5(10)-triene (6a). White solid: mp 140 °C; IR 1774, 176, 1376 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 7.22 (m, 4H), 3.58 (t, *J* = 8.5 Hz, 1H), 3.28 (d, *J* = 3.8 Hz, 1H), 2.91 (m, 2H), 2.84 (d, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), 1.98 (m, 6H), 1.55 (m, 3H), 1.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 208.4 (s), 177.8 (s), 137.2 (s), 134.5 (s), 129.7 (d), 126.5 (d)(2C), 126.3 (d), 95.4 (s), 56.8 (d), 51.5 (d), 43.9 (d), 37.3 (d), 35.6 (d), 34.2 (t), 32.1 (q), 28.1 (t), 27.1 (t), 24.8 (t), 24.5 (t). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.47; H, 7.07.

11α,13α-Carbolactone-17α-(2-oxoethyl)gona-1,3,5(10)-triene (7a). White solid: mp 102–103 °C; IR 1774, 1725, 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.80 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.14 (m, 3H), 3.24 (d, *J* = 4.3 Hz, 1H), 2.91 (m, 2H), 2.89 (dd, *J* = 18.4, 7.1 Hz, 1H), 2.74 (d, *J* = 10.5 Hz, 1H), 2.59 (dd, *J* = 18.4, 7.1 Hz, 1H), 2.47 (dq, *J* = 12.3, 7.1 Hz, 1H), 2.20 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.10 (m; 1H), 2.08 (d, *J* = 12.3 Hz, 1H), 1.99 (m, 2H), 1.85 (dt, *J* = 11.2, 7.2 Hz, 1H), 1.56 (m, 2H), 1.39 (dq, *J* = 12.3, 5.8 Hz, 1H), 1.10 (dq, *J* = 12.2, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 200.9 (d), 179.8 (s), 138.1 (s), 136.6 (s), 129.0 (d), 126.1 (d), 125.5 (d), 123.9 (d), 93.5 (s), 51.6 (d), 43.9 (t), 40.9 (d), 40.4 (d), 39.7 (d), 39.4 (d), 32.8 (t), 31.2 (t), 29.3 (t), 28.6 (t), 26.9 (t); MS *m/z* 310 (22), 268 (18), 267 (24), 266 (91), 222 (35), 221 (100), 129 (60), 115 (48).

17α-Acetyl-11α,13α-carbolactone-2-methoxygona-1,3,5(10)-triene (5b). White solid: mp 189 °C; IR 1774, 1706, 1376, 1275, 1042 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 7.17 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.57 (s, 3H), 3.15 (d, *J* = 4.8 Hz, 1H), 2.68 (m, 3H), 2.31 (dd, *J* = 10.6, 6.6 Hz, 1H), 2.06 (s, 3H), 1.78 (dd, *J* = 12.3, 4.8 Hz, 1H), 1.68 (m, 5H), 1.63 (d, *J* = 12.3 Hz, 1H), 1.15 (m, 2H), 0.56 (dq, *J* = 11.4, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 204.9 (s), 179.3 (s), 157.9 (s), 139.4 (s), 130.3 (d), 128.7 (s), 111.8 (d), 110.5 (d), 93.2 (s), 58.5 (d), 55.4 (q), 51.7 (d), 41.2 (d), 40.8 (d), 40.3 (d), 34.1 (t), 30.7 (q), 29.4 (t), 28.1 (t), 27.4 (t), 26.9 (t). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.11; H, 7.06. Found: C, 74.16; H, 7.20.

17β-Acetyl-11α,13α-carbolactone-2-methoxygona-1,3,5(10)-triene (6b). White solid: mp 152 °C; IR 1777, 1711, 1253, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.00 (d, *J* = 8.3 Hz, 1H), 6.82 (s, 1H), 6.70 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.78 (s, 3H), 3.55 (t, *J* = 8.4 Hz, 1H), 3.20 (br. d, *J* = 4.4 Hz, 1H), 2.77 (m, 3H), 2.24 (s, 3H), 2.22 (m, 1H), 1.91 (m, 7H), 1.45 (m, 2H), ; ^{13}C NMR ($CDCl_3$) δ 207.5 (s), 179.5 (s), 158.1 (s), 139.4 (s), 130.4 (d), 128.7 (s), 112.0 (d), 110.7 (d), 94.9 (s), 56.3 (d), 55.5 (q), 50.3 (d), 41.7 (d), 40.7 (d), 40.2 (d), 32.1 (q), 29.6 (t), 28.4 (t), 28.0 (t), 27.8 (t), 26.0 (t). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.11; H, 7.06. Found: 74.17; H, 7.02.

11α,13α-Carbolactone-2-methoxy-17α-(2-oxoethyl)gona-1,3,5(10)-triene (7b). White solid: mp 105 °C; IR 1774, 1723, 1189, 911 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.92 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.69 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.78 (s, 3H), 3.18 (d, *J* = 4.1 Hz, 1H), 2.89 (dd, *J* = 18.2, 6.7 Hz, 1H), 2.83 (m, 2H), 2.71 (d, *J* = 11.1 Hz, 1H), 2.69 (dd, *J* = 18.2, 6.8 Hz, 1H), 2.48 (dq, *J* = 11.2, 6.8 Hz, 1H), 2.21 (dd, *J* = 12.2, 4.1 Hz, 1H), 2.07 (d, *J* = 12.2 Hz, 1H), 2.06 (m, 3H), 1.84 (td, *J* = 10.6, 5.8 Hz, 1H), 1.53 (m, 2H), 1.38 (dq, *J* = 12.2, 5.8 Hz, 1H), 1.08 (dq, *J* = 12.2, 5.8 Hz, 1H), ; ^{13}C NMR ($CDCl_3$) δ 201.2 (d), 180.2 (s), 157.8 (s), 139.7 (s), 130.2 (d), 128.7 (s), 111.7 (d), 110.4 (d), 93.9 (s), 55.3 (q), 51.9 (d), 44.3 (t), 41.4 (d), 40.9 (d), 40.1 (d), 39.7 (d), 33.2 (t), 33.2 (t), 31.6 (t), 28.1 (t), 27.4 (t). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.11; H, 7.06. Found: 74.04; H, 7.15.

17α-Acetyl-11α,13α-carbolactone-2,3-dimethoxygona-1,3,5(10)-triene (5c). White solid: mp 180 °C; IR 1774, 1720, 1215, 1022 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 6.87 (s, 1H), 6.48 (s, 1H), 3.51 (s, 3H), 3.45 (s, 3H), 2.98 (d, *J* = 4.5 Hz, 1H), 2.61 (d, *J* = 10.9 Hz, 1H), 2.55 (m, 2H), 2.17 (dd, *J* = 10.6, 6.4 Hz, 1H), 1.99 (ddt, *J* = 12.9, 10.6, 6.4 Hz, 1H), 1.92 (s, 3H), 1.71 (m, 1H), 1.64 (dd, *J* = 12.2, 4.5 Hz, 1H), 1.55 (d, *J* = 12.2 Hz, 1H), 1.50 (m, 1H), 1.46 (td, *J* = 10.5, 6.3 Hz, 1H), 1.36 (dtd, *J* = 12.9, 6.4, 1.8 Hz, 1H), 1.10 (m, 1H), 1.08 (m, 1H), 0.49 (dq, *J* = 11.8, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 204.9 (s), 179.4 (s), 147.6 (s), 147.2 (s), 129.6 (s), 128.7 (s), 112.5 (d), 108.6 (d), 93.3 (s), 58.7 (d), 55.3 (q), 55.2 (q), 51.4 (d), 40.5 (d), 41.5 (d), 41.1 (d), 34.2 (t), 30.7 (q), 29.3 (t), 29.1 (t), 27.6 (t), 26.9 (t). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.03. Found: C, 71.22; H, 7.15.

17β-Acetyl-11α,13α-carbolactone-2,3-dimethoxygona-1,3,5(10)-triene (6c). White solid: mp 172-173 °C; IR 1775, 1715, 1230 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 6.48 (s, 1H), 6.33 (s, 1H), 3.47 (s, 3H), 3.41 (s, 3H), 3.25 (t, *J* = 4.7 Hz, 1H), 3.19 (t, *J* = 4.7 Hz, 1H), 3.02 (dd, *J* = 8.8, 4.7 Hz, 1H), 2.58 (dt, *J* = 16.7, 5.9 Hz, 1H), 2.27 (dd, *J* = 16.7, 4.9 Hz, 1H), 2.08 (m, 1H), 1.92 (m, 1H), 1.87 (m, 1H), 1.81 (m, 1H), 1.68 (m, 3H), 1.56 (s, 3H), 1.52 (m, 2H), 1.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 208.4 (s), 177.8 (s), 147.9 (s), 147.6 (s), 129.6 (s), 126.1 (s), 112.1 (d), 109.3 (d), 95.5 (s), 56.9 (d), 56.1 (q), 55.8 (q), 45.9 (d), 43.7 (d), 37.1 (d), 35.6 (d), 34.2 (t), 31.7 (q), 28.2 (t), 27.2 (t), 24.7 (t), 24.5 (t). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.03. Found: C, 71.30; H, 7.09.

11α,13α-Carbolactone-2,3-dimethoxy-17α-(2-oxoethyl)gona-1,3,5(10)-triene (7c). White solid: mp 161 °C; IR 1772, 1722, 1264 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.81 (s, 1H), 6.76 (s, 1H), 6.57 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.13 (d, *J* = 3.6 Hz, 1H), 2.89 (dd, *J* = 18.2, 6.8 Hz, 1H), 2.79 (m, 2H), 2.69 (d, *J* = 10.4 Hz, 1H), 2.59 (dd, *J* = 18.2, 6.9 Hz, 1H), 2.47 (m, 1H), 2.09 (m, 5H), 1.82 (m, 1H), 1.56 (m, 2H), 1.38 (dq, *J* = 11.8, 5.5 Hz, 1H), 1.14 (dq, *J* = 11.8, 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 201.2 (d), 180.3 (s), 147.6 (s), 147.1 (s), 129.9 (s), 128.7 (s), 112.4 (d), 108.5 (d), 94.0 (s), 56.2 (q), 55.9 (q), 51.6 (d), 44.4 (t), 41.6 (d), 41.2 (d), 40.4 (d), 39.9 (d), 33.3 (t), 31.6 (t), 29.6 (t), 29.1 (t), 27.6 (t). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.03. Found: C, 71.42; H, 7.15.

11α,13α-Carbolactone-11β-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene (10a). White solid: mp 115 °C; IR 1772, 1722, 1264 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.82 (s, 1H), 7.09 (m, 3H), 6.82 (d, J = 6.1 Hz, 1H), 3.70 (s, 3H), 3.09 (d, J = 11.0 Hz, 1H), 2.86 (m, 3H), 2.81 (d, J = 12.3 Hz, 1H), 2.62 (dd, J = 17.7, 7.8 Hz, 1H), 2.42 (dt, J = 12.1, 7.8 Hz, 1H), 2.27 (d, J = 12.3 Hz, 1H), 1.95 (m, 4H), 1.27 (m, 3H), 0.95 (dq, J = 11.4, 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 200.7 (d), 175.4 (s), 170.1 (s), 141.7 (s), 137.7 (s), 128.8 (d), 126.1 (d), 125.8 (d), 121.2 (d), 92.8 (s), 55.4 (s), 53.1 (q), 52.7 (d), 43.9 (t), 42.9 (d), 42.9 (d), 39.2 (d), 35.9 (t), 31.8 (t), 30.6 (t), 27.4 (t), 26.1 (t). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.74; H, 6.52. Found: C, 71.62; H, 6.60.

17α-Acetyl-11α,13α-carbolactone-2-methoxy-11β-methoxycarbonylgona-1,3,5(10)-triene (9b). White solid: mp 149 °C; IR 1781, 1726, 1357, 1260, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.02 (d, J = 8.2 Hz, 1H), 6.66 (m, 1H), 6.43 (s, 1H), 3.70 (s, 6H), 3.06 (d, J = 10.9 Hz, 1H), 2.94 (d, J = 12.4 Hz, 1H), 2.90 (d, J = 10.0 Hz, 1H), 2.69 (m, 2H), 2.47 (d, J = 12.4 Hz, 1H), 2.23 (s, 3H), 2.11 (m, 1H), 1.90 (m, 3H), 1.50 (m, 1H), 1.30 (m, 2H), 0.94 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 200.7 (s), 175.3 (s), 170.0 (s), 157.9 (s), 142.8 (s), 129.6 (s), 129.4 (d), 110.9 (d), 108.2 (d), 92.7 (s), 65.9 (s), 55.3 (d), 53.0 (q), 52.8 (q), 43.9 (d), 43.8 (d), 43.2 (d), 39.3 (t), 35.9 (t), 31.8 (q), 30.6 (t), 26.5 (t)(2C). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.34; H, 6.53. Found: C, 69.28; H, 6.51.

11α,13α-Carbolactone-2-methoxy-11β-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene (10b). White solid: mp 105 °C; IR 1778, 1725, 1166, 961 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.79 (s, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.67 (m, 1H), 6.42 (s, 1H), 3.69 (s, 6H), 3.05 (d, J = 9.9 Hz, 1H), 2.87 (dd, J = 18.0, 5.5 Hz, 1H), 2.77 (m, 3H), 2.48 (m, 1H), 2.28 (d, J = 12.4 Hz, 1H), 1.86 (m, 4H), 1.40 (m, 4H), 1.12 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 200.7 (s), 175.4 (s), 170.0 (s), 157.9 (s), 142.8 (s), 129.6 (s), 129.4 (d), 110.9 (d), 108.2 (d), 92.7 (s), 55.5 (s), 55.3 (d), 53.0 (q), 52.8 (q), 43.9 (t), 43.2 (d), 42.9 (d), 39.3 (d), 35.9 (t), 31.8 (t), 30.6 (t), 26.5 (t)(2C); MS m/z 398 (100), 322 (32), 278 (17), 237 (18), 249 (29), 159 (65). Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.22; H, 6.65.

17α-Acetyl-11α,13α-carbolactone-2,3-dimethoxy-11β-methoxycarbonyl-gona-1,3,5(10)-triene (9c). White solid: mp 137-138 °C; IR 1789, 1727, 1712, 1258, 914 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.63 (s, 1H), 6.52 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.65 (s, 3H), 3.07 (d, J = 11.1 Hz, 1H), 2.91 (dd, J = 10.2, 7.1 Hz, 1H), 2.79 (d, J = 12.5 Hz, 1H), 2.75 (t, J = 6.6 Hz, 2H), 2.57 (d, J = 12.5 Hz, 1H), 2.24 (s, 3H), 2.15 (m, 2H), 1.96 (ddd, J = 11.1, 7.1, 5.5 Hz, 1H), 1.87 (m, 2H), 1.50 (m, 1H), 1.41 (qd, J = 11.1, 5.5 Hz, 1H), 1.04 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 204.3 (s), 173.9 (s), 169.8 (s), 147.0 (s), 146.7 (s), 131.4 (s), 129.5 (s), 112.2 (d), 106.8 (d), 91.1 (s), 57.7 (d), 56.3 (s), 55.9 (q), 55.8 (q), 52.5 (d or q), 51.9 (q or d), 43.5 (d), 42.4 (d), 37.4 (t), 30.7 (q), 29.5 (t), 27.7 (t), 26.7 (t), 26.5 (t); MS m/z 428 (39), 352 (18), 307 (13), 305 (22), 281 (33), 273 (37), 43 (100). Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.29; H, 6.54. Found: C, 67.35; H, 6.65.

11α,13α-Carbolactone-2,3-dimethoxy-11β-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene (10c). White solid: mp 146 °C; IR 1790, 1720, 1260, 1150, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.83 (s, 1H), 6.62 (s, 1H), 6.50 (s, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.63 (s, 3H), 3.05 (d, J = 10.5 Hz, 1H), 2.88 (dd, J = 18.3, 6.1 Hz, 1H), 2.68 (dd, J = 18.3, 6.0 Hz, 1H), 2.59 (m, 4H), 2.28 (d, J = 12.4 Hz, 1H), 1.89 (m, 4H), 1.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 200.8 (d), 175.6 (s), 170.2 (s), 146.8 (s), 146.7 (s), 131.8 (s), 129.7 (s), 112.2 (d), 106.9 (d), 91.9 (s), 56.1 (d or q), 55.9 (q or d), 55.2 (s), 52.6 (q)(2C), 44.1 (t), 43.7 (d), 42.5 (d), 39.4 (d), 36.6 (t), 31.7 (t), 27.8 (t), 26.7 (t), 26.6 (t). Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.29; H, 6.54. Found: C, 67.38; H, 6.45.

17α-Acetyl-13α-hydroxy-11α-methoxycarbonylgona-1,3,5(10)-triene (12a). White solid: mp 120 °C; IR 3460, 3040, 1740, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.00 (m, 4H), 3.89 (s, 1H), 3.76 (s, 3H), 3.04 (br t, *J* = 10.4 Hz, 1H), 2.79 (m, 3H), 2.71 (dd, *J* = 10.7, 8.7 Hz, 1H), 2.18 (s, 3H), 1.99 (m, 6H), 1.65 (dt, *J* = 11.4, 5.1 Hz, 1H), 1.76-1.09 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 212.3 (s), 177.3 (s), 140.0 (s), 137.3 (s), 128.3 (d), 126.0 (d)(2C), 124.9 (d), 80.3 (s), 57.5 (q), 54.2 (d), 52.3 (d), 44.2 (d), 41.0 (d), 40.0 (d), 37.2 (t), 30.9 (q), 28.9 (t), 28.2 (q)(2C), 26.5 (t); MS *m/z* 324 (16), 280 (16), 264 (30), 222 (17), 221 (100), 220 (13), 141 (23), 129 (20), 128 (12), 115 (14), 91 (11), 71 (16), 64 (10), 57 (12), 55 (15), 44 (22), 43 (45), 41 (12); HRMS calcd for $C_{21}H_{26}O_4$, 342.1831, found, 342.1829.

13α-Hydroxy-11α-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene hemiacetal (13a) White wax; IR 3420, 3030, 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.87 (m, 4H), 5.49 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.04 (t, *J* = 10.6 Hz, 1H), 2.75 (m, 3H), 2.37-1.11 (m, 17H); ^{13}C NMR ($CDCl_3$) δ 176.9 (s), 140.5 (s), 138.0 (s), 127.9 (d), 125.8 (d), 125.7 (d), 99.4 (d), 94.7 (s), 53.0 (d), 52.0 (q), 44.9 (d), 44.6 (d), 40.3 (t), 40.2 (d), 38.7 (d), 31.0 (t), 29.4 (t), 28.8 (t), 28.5 (t); MS *m/z* 342 (7), 325 (12), 324 (54), 281 (17), 264 (29), 236 (19), 222 (26), 221 (100), 220 (80), 219 (20), 194 (27), 156 (30), 155 (12), 143 (15), 142 (19), 141 (37), 130 (19), 129 (42), 128 (41), 117 (24); HRMS calcd for $C_{21}H_{26}O_4$, 342.1831, found, 342.1819.

17α-Acetyl-13α-hydroxy-2-methoxy-11α-methoxycarbonylgona-1,3,5(10)-triene (12b). White solid: mp 112-113 °C; IR 3480, 1729, 1702, 1172 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.94 (d, *J* = 8.3 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.53 (d, *J* = 1.9 Hz, 1H), 3.87 (br s, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.97 (t, *J* = 10.2 Hz, 1H), 2.71 (m, 5H), 2.15 (m, 1H), 2.14 (s, 3H), 1.93 (s, 3H), 1.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 212.3 (s), 177.3 (s), 157.9 (s), 141.5 (s), 129.9 (s), 129.1 (d), 111.3 (d), 111.2 (d), 80.3 (s), 57.7 (d), 55.2 (q), 54.3 (q), 52.4 (d), 44.3 (d), 41.3 (d), 40.1 (d), 37.2 (t), 31.1 (q), 28.5 (t), 28.3 (t), 28.1 (t), 26.5 (t). Anal. Calcd for $C_{21}H_{28}O_5$: C, 70.97; H, 7.13. Found: C, 70.85; H, 7.70.

13α-Hydroxy-2-methoxy-11α-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene hemiacetal (13b). White wax; IR 3400, 3013, 1727, 1611, 1215, 1042 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.94 (d, *J* = 8.2 Hz, 1H), 6.59 (m, 2H), 5.51 (m, 1H), 3.97 (br s, 1H), 3.70 (s, 3H), 3.67 (s. 3H), 2.98 (t, *J* = 10.2 Hz, 1H), 2.72 (m, 3H), 1.62 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 177.1 (s), 157.9 (s), 142.0 (s), 130.2 (s), 128.9 (d), 111.5 (d), 111.2 (d), 100.0 (d), 95.0 (s), 55.3 (q), 53.4 (d), 52.2 (d), 45.8 (d or q), 45.1 (q or d), 41.4 (t), 40.5 (d), 39.0 (d), 36.6 (t), 31.3 (t), 30.2 (t), 29.1 (t), 28.3 (t).

17α-Acetyl-2,3-dimethoxy-13α-hydroxy-11α-methoxycarbonylgona-1,3,5(10)-triene (12c). White solid: mp 150 °C; IR 3520, 3070, 1730, 1260, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.59 (s, 2H), 3.97 (br s, 1H), 3.84 (s, 6H), 3.79 (s, 3H), 3.00 (t, *J* = 6.3 Hz, 1H), 2.73 (m, 4H), 2.21 (m, 1H), 2.20 (s, 3H), 2.14 (s, 3H), 1.70 (m, 2H), 1.44 (m, 2H), 1.18 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 212.2 (s), 177.7 (s), 147.0 (s), 146.9 (s), 131.8 (s), 129.7 (s), 111.5 (d), 109.2 (t), 80.3 (s), 57.9 (d), 57.7 (q), 55.8 (q), 54.0 (q), 52.3 (d), 44.8 (d), 41.1 (d), 40.5 (d), 37.2 (t), 31.0 (q), 28.5 (t), 28.4 (t), 28.3 (t), 26.5 (t). Anal. Calcd for $C_{23}H_{30}O_6$: C, 68.66; H, 7.46. Found: C, 68.70; H, 7.43.

2,3-Dimethoxy-13α-hydroxy-11α-methoxycarbonyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene hemiacetal (13c). White wax; IR 3450, 3050, 1730, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.53 (s, 2H), 5.51 (m, 1H), 3.76 (s, 3H), 3.70 (s, 6H), 3.18 (br s, 1H), 2.96 (dt, *J* = 11.2, 7.0 Hz, 1H), 2.68 (m, 3H), 1.75 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 177.6 (s), 147.0 (s), 146.9 (s), 132.3 (s), 130.0 (s), 111.4 (d), 109.4 (d), 100.0 (d), 95.0 (s), 55.9 (q), 55.8 (q), 52.5 (d or q), 52.2 (q or d), 45.6 (d), 45.4 (d), 41.3 (t), 40.3 (d), 39.8 (d), 39.3 (t), 29.1 (t), 29.0 (t), 28.9 (t), 28.8 (t).

17α-Acetyl-13α-hydroxy-11,11-bis(methoxycarbonyl)gona-1,3,5(10)-triene (15). White solid: mp 137 °C; IR 3420, 1740, 1712, 1160 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.44 (t, J = 3.9 Hz, 1H), 7.03 (m, 3H), 3.74 (d, J = 10.8 Hz, 1H), 3.88 (s, 3H), 3.43 (br s, 1H), 3.21 (s, 3H), 3.03 (d, J = 14.1 Hz, 1H), 2.79 (m, 2H), 2.49 (dd, J = 11.9, 6.5 Hz, 1H), 2.24 (d, J = 14.1 Hz, 1H), 2.20 (s, 3H), 1.89 (m, 7H), 1.32 (dq, J = 11.5, 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 211.4 (s), 174.5 (s), 172.2 (s), 138.0 (s), 136.6 (s), 128.7 (d), 128.6 (d), 125.7 (d), 125.3 (d), 79.1 (s), 62.0 (d), 59.4 (s), 55.5 (q), 52.9 (q), 51.9 (d), 44.3 (d), 42.4 (t), 39.9 (d), 30.8 (t), 30.6 (t), 30.3 (q), 27.8 (t), 27.2 (t); MS *m/z* 400 (4), 382 (17), 369 (19), 339 (11), 325 (23), 323 (54), 322 (15), 292 (18), 291 (21), 290 (29), 280 (19), 279 (59), 219 (52), 207 (27), 195 (30), 193 (20), 179 (17), 167 (18), 155 (29), 141 (46), 130 (25), 129 (53), 128 (36), 117 (22), 115 (29), 91 (27), 55 (18), 44 (43), 43 (100); HRMS calcd for $C_{23}H_{28}O_6$, 400.1885, found, 400.1871.

13α-Hydroxy-11,11-bis(methoxycarbonyl)-17α-(2-oxoethyl)gona-1,3,5(10)-triene hemiacetal (16). White solid: mp 145 °C; IR 3420, 3030, 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.45 (m, 1H), 7.00 (m, 3H), 5.47 (m, 1H), 3.82 (s, 3H), 3.77 (m, 1H), 3.15 (s, 3H), 2.75 (m, 3H), 2.52 (m, 1H), 2.22 (d, J = 14.2 Hz, 1H), 2.17-1.60 (m, 9H), 1.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 174.8 (s), 172.1 (s), 138.3 (s), 136.5 (s), 129.1 (d), 128.7 (d), 125.6 (d), 125.1 (d), 101.2 (d), 93.0 (s), 59.9 (s), 53.6 (q), 52.2 (q), 51.7 (d), 49.3 (d), 44.2 (d), 41.1 (t), 39.9 (d), 38.9 (t), 32.9 (t), 31.6 (t).

17α-Acetyl-13α-hydroxy-11α-hydroxymethylgona-1,3,5(10)-triene (18). White solid: mp 123 °C; IR 3520, 3050, 1710, 1212, 1135 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 7.32 (d, J = 6.6 Hz, 1H), 7.24 (m, 3H), 4.74 (br s, 1H), 3.92 (m, 1H), 3.84 (dd, J = 11.2, 2.1 Hz, 1H), 3.58 (br s, 1H), 2.82 (dd, J = 11.8, 7.5 Hz, 1H), 2.69 (m, 2H), 2.59 (dd, J = 11.2, 2.12 Hz, 1H), 2.21 (m, 1H), 1.86 (m, 1H), 1.94 (dd, J = 14.3, 6.4 Hz, 1H), 1.86 (dd, J = 14.6, 2.8 Hz, 1H), 1.73 (s, 3H), 1.63 (m, 1H), 1.62 (m, 1H), 1.60 (dd, J = 14.3, 7.5 Hz, 1H), 1.43 (dq, J = 11.9, 5.4 Hz, 1H), 1.18 (m, 1H), 0.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 213.6 (s), 141.6 (s), 137.2 (s), 128.7 (d), 125.9 (d), 125.6 (d), 125.5 (d), 80.7 (s), 68.0 (t), 61.6 (s), 53.3 (d), 40.8 (d), 40.1 (d), 39.4 (d), 39.1 (t), 31.1 (q), 30.0 (t), 29.8 (t), 28.1 (t), 27.6 (t). Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.43; H, 8.28. Found: C, 76.37; H, 8.35.

13α-Hydroxy-11α-hydroxymethyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene bis-acetal (19). White solid: mp 219 °C; IR 1677, 1650, 1087, 1022 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 8.3 Hz, 2H), 7.20 (m, 2H), 7.12 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 7.4 Hz, 2H), 5.33 (dd, J = 8.8, 2.4 Hz, 2H), 4.92 (dd, J = 10.3, 8.8 Hz, 2H), 3.74 (br d, J = 10.8 Hz, 2H), 3.48 (q, J = 8.3 Hz, 2H), 2.65 (m, 6H), 2.24 (m, 6H), 1.99 (dq, J = 14.8, 6.4 Hz, 2H), 1.85 (dt, J = 8.8, 2.4 Hz, 2H), 1.76 (m, 4H), 1.56 (m, 4H), 1.27 (m, 4H), 1.13 (m, 2H), 1.03 (qd, J = 11.4, 4.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 141.6 (s), 137.7 (s), 128.4 (d), 126.1 (d), 125.6 (d)(2C), 106.8 (d), 95.3 (s), 73.9 (t), 53.6 (d), 51.4 (d), 41.0 (d), 39.3 (d), 38.9 (d), 38.3 (t), 33.6 (t), 31.5 (t), 30.2 (t), 29.7 (t), 29.3 (t); MS *m/z* 592 (3), 575 (19), 574 (41), 296 (17), 261 (22), 253 (47), 251 (100), 236 (37), 235 (88), 234 (48), 233 (31), 223 (48), 221 (52), 141 (69), 139 (57), 117 (96).

17α-Acetyl-13α-hydroxy-11α-hydroxymethylgona-1,3,5(10)-triene diphenylsilyldioxy (21). White solid: mp 140 °C; IR 3058, 1715, 1650, 1264, 1069 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 7.86 (m, 5H), 7.17 (m, 9H), 4.17 (br d, J = 11.3 Hz, 1H), 3.96 (m, 1H), 3.14 (m, 1H), 2.65 (m, 2H), 2.21 (m, 2H), 2.16 (s, 3H), 2.07–1.01 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 209.9 (s), 141.7 (s), 136.8 (s), 134.8 (d)(3C), 134.4 (d)(2C), 130.3, 130.2, 129.1, 128.0 (d)(2C), 127.9 (d)(3C), 126.1, 125.7, 125.6, 87.1 (s), 70.8 (t), 65.4 (d), 54.5 (d), 41.7 (d), 41.2 (d), 41.1 (t), 39.8 (d), 31.1 (q), 30.3 (t), 30.1 (t), 27.8 (t), 27.4 (t). Anal. Calcd for $C_{32}H_{34}O_3Si$: C, 82.37; H, 7.34. Found: C, 82.38; H, 7.01.

13α-Hydroxy-11α-hydroxymethyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene diphenylsilyldioxy (22). White solid: mp 92–93 °C; IR 3058, 1720, 1650, 1264, 1069 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 9.92 (s, 1H), 7.44 (m, 14H), 4.25 (m, 2H), 3.13 (m, 1H), 2.85 (m, 4H), 2.56 (m, 1H), 2.37–1.09 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 203.1 (d), 141.7 (s), 137.0 (s), 135.1 (s), 134.8 (d)(2C), 134.4 (d)(2C), 130.4, 130.1, 129.2, 128.1 (d)(3C), 127.9 (d)(2C), 126.1, 125.7, 125.5, 85.6 (s), 71.0 (t), 53.9 (d), 47.7 (t), 43.9, 41.7, 41.0, 40.9, 40.5, 30.3 (t), 30.2 (t), 29.8 (t), 27.8 (t).

17α-Acetyl-13α-hydroxy-11α-benzyloxymethylgona-1,3,5(10)-triene (24). White solid: mp 117–118 °C; IR 3490, 3050, 1694, 1265, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.29 (m, 5H), 7.09 (m, 4H), 4.58 (1/2AB, J = 12.2 Hz, 1H), 4.54 (1/2AB, J = 12.2 Hz, 1H), 4.16 (br s, 1H), 3.79 (1/2AB d, J = 9.2, 3.4 Hz, 1H), 3.74 (1/2AB d, J = 9.2, 6.5 Hz, 1H), 2.76 (m, 2H), 2.59 (dd, J = 11.3, 7.9 Hz, 1H), 2.38 (m, 1H), 2.33 (dd, J = 11.1, 9.7 Hz, 1H), 2.19 (m, 1H), 2.19 (s, 3H), 2.06 (m, 3H), 1.93 (m, 2H), 1.64 (dt, J = 11.8, 6.9 Hz, 1H), 1.27 (m, 1H), 1.14 (m, 1H), 1.13 (dq, J = 9.7, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 212.1 (s), 141.4 (s), 138.3 (s), 138.1 (s), 128.5 (d), 128.3 (d), 127.8 (d), 127.7 (d), 125.7 (d), 125.3 (d), 80.8 (s), 75.2 (t), 73.4 (t), 60.4 (d), 54.6 (d), 41.1 (d), 41.0 (d), 37.8 (d), 37.6 (t), 31.1 (q), 29.2 (t), 28.2 (t), 26.9 (t); MS *m/z* 404 (1), 296 (12), 278 (28), 235 (20), 170 (24), 155 (10), 141 (18), 129 (22), 128 (17), 91 (100), 43 (65).

13α-Hydroxy-11α-benzyloxymethyl-17α-(2-oxoethyl)gona-1,3,5(10)-triene (25). White solid: mp 90–91 °C; IR 3404, 3055, 1264, 1089, 1020, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33 (m, 5H), 7.11 (m, 4H), 5.50 (m, 1H), 4.60 (m, 2H), 3.83 (m, 2H), 2.75 (m, 3H), 2.40 (m, 2H), 2.05 (m, 8H), 1.73 (m, 1H), 1.36 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 141.5 (s), 141.4 (s), 138.0 (s), 128.5 (d), 128.4 (d), 128.3 (d), 128.0 (d), 127.9 (d), 127.7 (d), 125.9 (d), 125.7 (d), 125.6 (d), 99.9 (d), 95.4 (s), 74.7 (t), 73.1 (t), 53.4 (d), 48.3 (t), 41.6 (d), 40.7 (d), 39.1 (d), 37.6 (d), 34.6 (t), 31.8 (t), 30.3 (t), 29.4 (t), 28.8 (t). Anal. Calcd for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.25; H, 7.80.

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