A Straightforward Synthesis of Cyclopropanes from Aldehydes and Ketones

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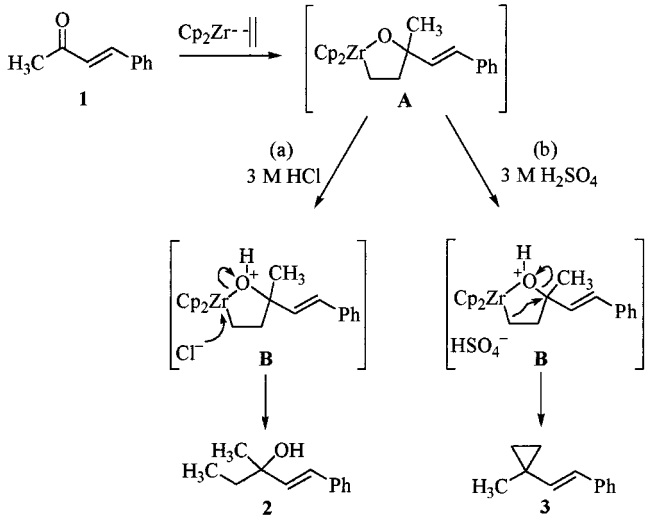
Keywords: Aldehydes / Cyclopropanes / Ketones / Lewis acids / Zirconium

A new synthetic methodology for preparing cyclopropanes is presented. The reaction involves a cooperative zirconium- and Lewis acid-mediated deoxygenative coupling of carbonyl compounds with a Grignard reagent. In this way, various cyclopropanes are obtained in moderate to excellent yields, directly from saturated, unsaturated, and aromatic aldehydes and ketones. This reaction tolerates the presence of several different functional groups.

Introduction

Development of new synthetic reactions aimed at interconverting important classes of compounds is of continuing interest. In this context, we have recently reported[1] a new procedure for obtaining vinylcyclopropanes.[2] Unlike the conventional cyclopropanation methods using a precursor C=C double bond,[2,3] this reaction involves α,β-unsaturated ketones as substrates. Thus, benzylideneacetone (**1**) reacts with zirconocene(ethylene) complex[4] to afford the intermediate oxazirconacyclopentane **A** which, depending upon hydrolysis conditions, could be selectively converted into either alcohol **2** (3 M HCl) or vinylcyclopropane **3** (3 M H_2SO_4) (Scheme 1). Various vinylcyclopropanes, including spiro compounds, were obtained predominantly or exclusively when sulfuric acid was used for protonolysis.

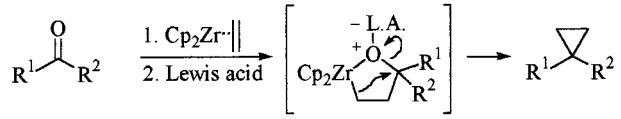


Scheme 1. Synthesis of vinylcyclopropanes under specific protic conditions

Certain limitations in the scope of the reaction were discovered. In particular, no ring-contraction occurred when starting from saturated or aryl ketones or α,β-enones containing a terminal conjugated C=C double bond; only the corresponding alcohols (analogous to **2**) were isolated in these cases. These limitations prompted us to study the reaction further. As a result of this research, we report here a much more general synthetic method that provides simple access to a wide range of cyclopropanes, directly from carbonyl compounds.

Results and Discussion

We have extended the cyclopropanation reaction significantly, thanks to an important modification to the original procedure. Our reasoning was initially based on the dichotomous behaviour of the two strong protic acids: 3 M HCl and 3 M H_2SO_4. We assumed that, in both cases, the initially formed oxazirconacyclopentane **A** had to be protonated to give the oxonium intermediate **B** (Scheme 1). Thereafter, in the presence of a weakly nucleophilic counter anion (HSO_4^-), deoxygenative ring contraction (path b) would compete favourably with Zr−O bond breaking (alternatively promoted by the more nucleophilic Cl^-, path a). Following this rationale, we envisioned Lewis acid-base interaction as the model for the specific activation of oxazirconacycle **A** by H_2SO_4. Consequently, we speculated that Lewis acids might behave in a similar fashion; i.e. activate the complex toward ring contraction (Scheme 2). The absence of water should also be beneficial to this reaction.



Scheme 2. Lewis acid-promoted contraction of the oxazirconacycle

The results obtained confirmed the above hypothesis. After initial optimisation of the experimental conditions, the cyclopropanation reaction took place as expected. In a typical experiment, Cp_2ZrEt_2 was produced from Cp_2ZrCl_2 and two equivalents of EtMgBr in THF at −78 °C, and Cp_2Zr(ethylene) generated by warming the reaction mixture to 0 °C.[4,5] The carbonyl compound was then added and the reaction allowed to proceed at room temperature. After

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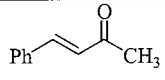
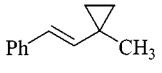
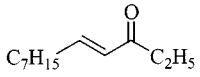
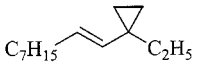
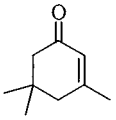
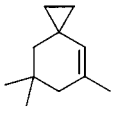
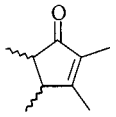
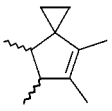
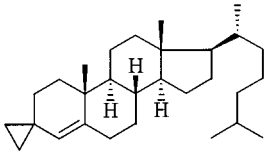
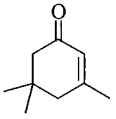
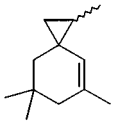
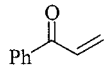
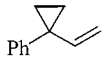
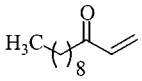
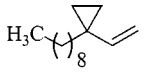
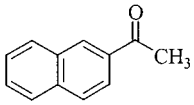
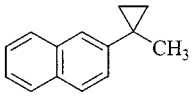
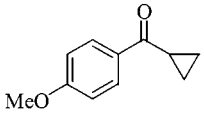
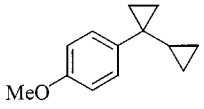
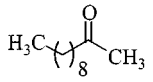
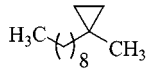
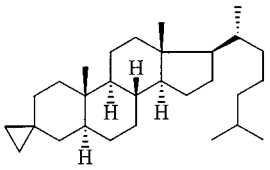
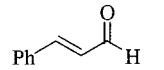
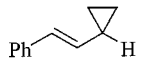
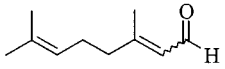
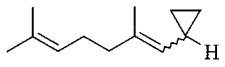
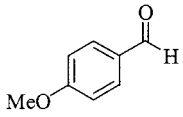
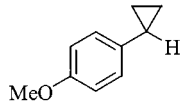
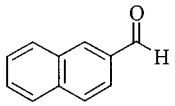
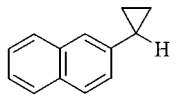
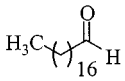
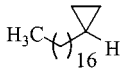
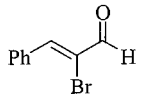
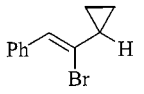
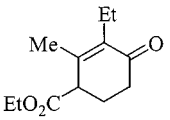
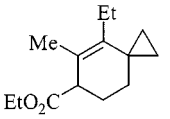
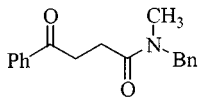
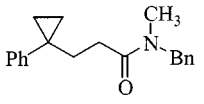
Table 1. Deoxygenative coupling of aldehydes and ketones with EtMgBr, promoted by Zr^{II} and $TiCl_4$

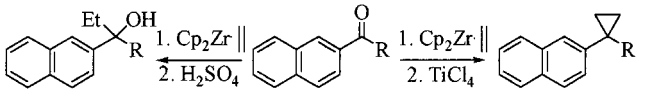
Entry	Carbonyl Compound	Product	Yield (%) [b],[c]
1	 **1**	 **3**	50 (45)
2	 **4**	 **5**	60 (31)
3	 **6**	 **7**	81 (75)
4	 **8** [d]	 **9** [d]	70 (55)
5	Cholest-4-en-3-one **10**	 **11**	90 (91)
6	 **6**	 **12** [a],[e]	50 (49)
7	 **13**	 **14**	71 (0)
8	 **15**	 **16**	40 (0)
9	 **17**	 **18**	64 (0)
10	 **19**	 **20**	70
11	 **21**	 **22**	42

Entry	Carbonyl Compound	Product	Yield (%) [b],[c]
12	Cholestan-3-one **23**	 **24**	36
13	 **25**	 **26**	75 (0)
14	 **27** [d]	 **28** [d]	71
15	 **29**	 **30**	88
16	 **31**	 **32**	58 (0)
17	 **33**	 **34**	21
18	 **35**	 **36**	56
19	 **37**	 **38**	72
20	 **39**	 **40**	69

[a] *n*PrMgBr was used instead of EtMgBr. – [b] Yields of isolated products. – [c] Yields for the reactions employing H_2SO_4 are given in parentheses. – [d] Mixture of isomers. – [e] 1:1 mixture of diastereoisomers.

the removal of THF in vacuo, the ring-contraction step proceeded in CH_2Cl_2 in the presence of a Lewis acid (1 equiv.). Among several Lewis acids tested, the best yields were generally observed when using $TiCl_4$ and $BF_3{\cdot}OEt_2$. The reaction appeared to be a synthetically attractive method: various carbonyl compounds, including unsaturated, saturated and aromatic ketones and aldehydes, could readily be transformed into the corresponding cyclopropanes.

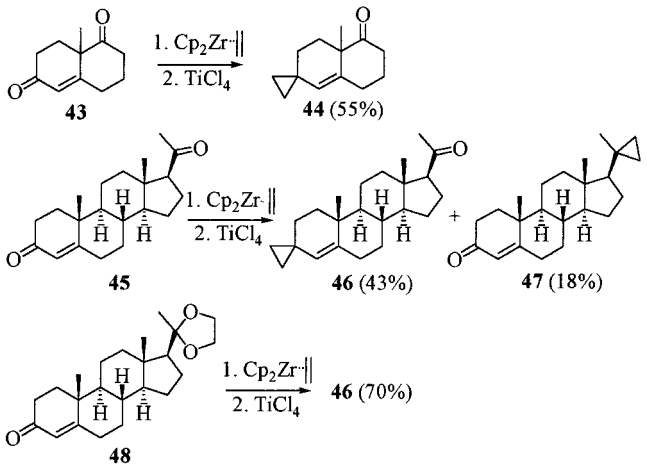
Table 1 summarises the results of reactions employing different carbonyl compounds, together with EtMgBr (or *n*PrMgBr) as a Grignard reagent and $TiCl_4$ as a Lewis acid promoter. Several outstanding features should be pointed out. α,β-Unsaturated ketones generally gave higher yields and cleaner reactions than under the original procedure using H_2SO_4 (entries 1−6). Moreover, the Lewis acid-based reactions also took place when α,β-enones containing a conjugated terminal double bond were used (entries 7 and 8). Most importantly, and in sharp contrast to the procedure using H_2SO_4, cyclopropane derivatives could be prepared in moderate to good yields from aromatic (**17** and **19**) and alkyl (**21** and **23**) ketones (entries 9−12). In this context, the easy preparation of bis-cyclopropane **20** should be noted (entry 10).[6] It also proved possible to prepare a substituted cyclopropane derivative **12** from Cp_2Zr(propene), like with the H_2SO_4-promoted preparation, by stabilizing the complex with PMe_3 (entry 6).[1] Unlike the H_2SO_4-based reaction, the Lewis acid-promoted cyclopropanation can also be accomplished starting from various aldehydes. Whereas the unsaturated (**25** and **27**) and aromatic (**29** and **31**) aldehydes afforded cyclopropane derivatives in good yields (entries 13−16), a considerably lower yield (21%) was found for the less reactive aliphatic aldehyde **33** (entry 17). As a general rule, the saturated carbonyl compounds gave lower yields than their unsaturated and aromatic analogues. (entries 11 vs. 2 or 12 vs. 5). This trend can be rationalised by assuming that, during the ring-contraction, the partial positive charge developing on the carbon α to oxygen is stabilized by adjacent unsaturation (Scheme 2). In contrast to the H_2SO_4-based procedure, no alcohols were formed from saturated or aromatic aldehydes and ketones when using $TiCl_4$. For instance, while the alcohols **41**[7] and **42**[7] were formed exclusively from ketone **17** and aldehyde **31** when treated with H_2SO_4, only the corresponding cyclopropanes **18** and **32** were obtained when using $TiCl_4$ (Scheme 3).



41 : R = Me (58%) **42** : R = H (70%) **17** : R = Me **31** : R = H **18** : R = Me (64%) **32** : R = H (58%)

Scheme 3. Reaction of the aromatic aldehydes and ketones: marked reactivity difference between H_2SO_4 and $TiCl_4$

The reaction described is compatible with the presence of several functional groups. Isolated C=C double bonds, ether, halogen, ester and amide groups can be present in the substrate and tolerated by an equivalent of the reagent (entries 14, 15, 18, 19 and 20). The higher chemoselectivity of the amide compared to that of the ester group was deduced from two additional competition experiments. Under typical reaction conditions, the equimolar mixture of enone **6** and methyl stearate afforded vinylcyclopropane **7** and 1-heptadecylcyclopropanol[8] in a 7:3 ratio. In the second experiment, employing **6** together with *N*-methyl-*N*-benzylacetamide, the latter was entirely recovered. Competing cyclopropanation has also been examined for the saturated and unsaturated ketones. As outlined in Scheme 4, in the case of the bicyclic diketone **43**, total chemoselectivity in favour of the more reactive enone functionality was observed. However, a mixture of two cyclopropane derivatives **46** and **47** was formed from progesterone (**45**), with a more easily accessible saturated ketone entity. A selective cyclopropanation on C3 could be achieved when using the acetal-monoprotected progesterone **48**. Interestingly, the deprotection on C-20 took place spontaneously in this reaction, to afford **46** cleanly.



Scheme 4. Competing cyclopropanations with saturated and α,β-unsaturated ketones

Conclusion

Conversion of zirconacycles into carbocycles is of particular interest from the synthetic point of view. However, the methods applied usually involve the replacement of zirconium with carbon.[9] The discovered reaction represents another approach: a deoxygenative contraction of an oxazirconacycle into a carbocycle. Thus, under cooperative zirconium and Lewis acid activation conditions, various ketones and aldehydes coupled with a Grignard reagent to afford cyclopropanes directly, in moderate to excellent yields. Easy access to spiro cyclopropane derivatives, compatibility with the presence of several different functional groups and relatively mild reaction conditions should encourage synthetic applications of this new cyclopropanation reaction.

Experimental Section

General: All reactions were carried out under argon using vacuum line techniques. THF was distilled under argon from sodium-benzophenone ketyl. Dichloromethane was distilled under argon over calcium hydride. Carbonyl substrates **13**,[10] **15**[11] and **33**[12] were prepared according to the described procedures, or obtained as below (compounds **4** and **39**). Zirconocene dichloride was purchased from Strem Chemicals. Other substrates and reagents were purchased from Aldrich. NMR spectra were recorded in $CDCl_3$ using Bruker AC 250 and DRX 500 spectrometers. High and low

resolution mass spectra were obtained on a GC-coupled instrument by the EI (70 eV) technique. Column flash chromatography was performed on silica gel 40−63 μm (Merck). Melting points were determined with a Büchi capillary apparatus and were not corrected.

(*E*)-4-Dodecen-3-one (4): To a 0.5 M solution of (*E*)-2-decenal (3.1 g, 20 mmol) in THF was added ethylmagnesium bromide (1 M in THF, 1.2 equiv.) at 0 °C. After completion of the reaction (ca. 1 hour), the mixture was quenched with 3 M HCl and extracted with ether. The combined organic layers were washed with saturated $NaHCO_3$, dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was distilled to give the pure alcohol, which was then oxidized with pyridinium chlorochromate (10.8 g, 50 mmol) in dichloromethane (0.5 M solution) at room temperature. Filtration, evaporation of the solvent and column chromatography purification gave **4** as a light yellow oil (2.2 g, 61%). − ^{1}H NMR (250 MHz): δ = 6.83 (dt, *J* = 15.8, 6.9 Hz, 1 H), 6.08 (dd, *J* = 15.8, 0.6 Hz, 1 H), 2.56 (q, *J* = 7.3 Hz, 2 H), 2.20 (q, *J* = 7.1 Hz, 2 H), 1.50−1.39 (m, 2 H), 1.35−1.20 (m, 8 H), 1.09 (t, *J* = 7.3 Hz, 3 H), 0.87 (t, *J* = 6.5 Hz, 3 H). − ^{13}C NMR (62.5 MHz): δ = 201.1 (Cq), 147.1 (CH), 129.9 (CH), 33.1 (CH_2), 32.4 (CH_2), 31.7 (2 CH_2), 29.0 (CH_2), 28.1 (CH_2), 22.5 (CH_2), 14.0 (CH_3), 8.1 (CH_3). − MS (70 eV); *m*/*z* (%): 182 (4) [$M^{+\cdot}$], 153 (100), 57 (82).

3-Benzoyl-*N*-benzyl-*N*-methylpropionamide[13] (39): β-Benzoylpropionic acid[14] (3.6 g, 20 mmol) and *N*-methylbenzylamine (2.2 g, 18 mmol) were coupled with the aid of dicyclohexylcarbodiimide according to the literature procedure.[15] The crude product was purified by column chromatography and recrystallisation from ethanol to give **39** (4.9 g, 85%, mixture of rotamers). − ^{1}H NMR (250 MHz): δ = 8.03−7.98 (m, 2 H), 7.60−7.20 (m, 8 H), 4.63, 4.61 (2s, 2 H), 3.41, 3.37 (2t, *J* = 6.5 Hz, 2 H), 3.00, 2.96 (s, 3 H), 2.85, 2.84 (2t, *J* = 6.5 Hz, 2 H). − ^{13}C NMR (62.5 MHz): δ = 199.0 (Cq), 171.9 (Cq), 171.7 (Cq), 137.2 (Cq), 136.7 (Cq), 136.4 (Cq), 132.9 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 126.3 (CH), 53.1 (CH_2), 50.8 (CH_2), 34.6 (CH_3), 33.8 (CH_3), 33.6 (CH_2), 27.3 (CH_2), 26.0 (CH_2).

General Procedure for the Synthesis of Cyclopropanes: To a solution of Cp_2ZrCl_2 (292 mg, 1 mmol) in THF (4 mL) was added EtMgBr (2 mL, 2 mmol, 1 M THF solution) at −78 °C. The green solution was stirred for 15 min at −78 °C and warmed to 0 °C until it turned red (10 min). The carbonyl compound (1 mmol in 2 mL of THF) was then added and the reaction was allowed to proceed at room temperature for 1−2 h. At this stage, H_2SO_4- or Lewis acid-induced ring-contraction might follow.

H_2SO_4-Based Protocol: 3 M H_2SO_4 (1 mL) was added with a syringe and the reaction mixture was stirred at room temperature for 5 min. The solution was diluted with Et_2O and treated with saturated aqueous $NaHCO_3$. The Et_2O layer was separated and the aqueous layer was extracted with Et_2O. The combined organic fractions were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography.

Lewis Acid-Based Protocol: THF was removed in vacuo from the reaction mixture. Dichloromethane (ca. 5 mL) was added, followed by $TiCl_4$ (1 mmol), and the reaction was allowed to proceed at room temperature for 20 min. A saturated aqueous solution of NH_4Cl was added and the mixture was extracted twice with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, and then dried over $MgSO_4$. The solution was concentrated under reduced pressure and the crude product was purified by flash chromatography.

(*E*)-β-(1-Methylcyclopropyl)styrene (3): Yield 79 mg (50%), colourless oil. − IR (film): $\tilde{\nu}$ = 3082 cm^{-1}, 2999, 2937, 2874, 1647, 1604, 1495, 1454. − ^{1}H NMR (250 MHz): δ = 7.40−7.13 (m, 5 H), 6.34 (d, *J* = 15.6 Hz, 1 H), 5.85 (d, *J* = 15.6 Hz, 1 H), 1.31 (s, 3 H), 0.73−0.67 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 138.7 (CH), 137.9 (Cq), 128.5 (2 CH), 126.5 (CH), 125.6 (2 CH), 125.4 (CH), 21.4 (CH_3), 17.8 (Cq), 15.6 (2 CH_2). − MS (70 eV); *m*/*z* (%): 158 (17) [$M^{+\cdot}$], 143 (100), 128 (96). − HRMS, $C_{12}H_{14}$: calcd. 158.1096; found 158.1127.

(*E*)-1-Ethyl-1-(1-nonenyl)cyclopropane (5): Yield 116 mg (60%), colourless oil. − IR (film): $\tilde{\nu}$ = 3083 cm^{-1}, 2961, 2922, 2860, 1466. − ^{1}H NMR (250 MHz): δ = 5.32 (d, *J* = 15.4 Hz, 1 H), 5.20 (dt, *J* = 15.4, 6.3 Hz, 1 H), 1.99−1.92 (m, 2 H), 1.43−1.17 (m, 12 H), 0.96−0.84 (m, 6 H), 0.48−0.44 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 134.8 (CH), 127.3 (CH), 32.6 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 22.6 (Cq), 14.1 (CH_2), 13.4 (2 CH_2), 11.1 (CH_3). − MS (70 eV); *m*/*z* (%): 194 (60) [$M^{+\cdot}$], 165 (90), 109 (100). − HRMS, $C_{14}H_{26}$: calcd. 194.2035; found 194.2014.

5,7,7-Trimethylspiro[2.5]oct-4-ene (7): Yield 120 mg (81%), colourless oil. − IR (film): $\tilde{\nu}$ = 2937 cm^{-1}, 2853, 1462, 1379. − ^{1}H NMR (250 MHz): δ = 4.72 (s, 1 H), 1.76 (s, 2 H), 1.65 (s, 3 H), 1.24 (s, 2 H), 0.97 (s, 6 H), 0.49−0.43 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 131.6 (Cq), 127.5 (CH), 46.0 (CH_2), 44.3 (CH_2), 31.1 (Cq), 28.7 (2 CH_3), 23.6 (CH_3), 17.3 (Cq), 13.3 (2 CH_2). − MS (70 eV); *m*/*z* (%): 150 (66) [$M^{+\cdot}$], 135 (100), 107 (97). − HRMS, $C_{11}H_{18}$: calcd. 150.1409; found 150.1399.

4,5,6,7-Tetramethylspiro[2.4]hept-4-ene (9): Yield 59 mg (70%, 85:15 mixture of isomers), yellow oil. *Major isomer*: ^{1}H NMR (500 MHz): δ = 2.12−2.08 (m, 1 H), 1.66−1.61 (m, 1 H), 1.60 (s, 3 H), 1.27 (s, 3 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 0.79 (d, *J* = 6.9 Hz, 3 H), 0.71−0.67 (m, 1 H), 0.63−0.59 (m, 1 H), 0.36 (ddd, *J* = 9.6, 6.3, 4.7 Hz, 1 H), 0.24 (ddd, *J* = 9.6, 6.2, 4.3 Hz, 1 H). − ^{13}C NMR (125 MHz): δ = 133.8 (Cq), 131.8 (Cq), 50.1 (CH), 45.3 (CH), 33.9 (Cq), 18.4 (CH_3), 16.0 (CH_3), 12.5 (CH_3), 9.0 (CH_3), 7.8 (CH_2), 5.0 (CH_2). − MS (70 eV); *m*/*z* (%): 150 (31) [$M^{+\cdot}$], 135 (100). *Minor isomer*: ^{1}H NMR (500 MHz): δ = 2.48 (quint, *J* = 7.2 Hz, 1 H), 2.24 (quint, *J* = 7.4 Hz, 1 H), 1.64 (s, 3 H), 1.27 (s, 3 H), 0.86 (d, *J* = 7.1 Hz, 3 H), 0.67 (d, *J* = 7.1 Hz, 3 H), 0.60−0.56 (m, 1 H), 0.53−0.49 (m, 1 H), 0.38−0.33 (m, 1 H), 0.28−0.23 (m, 1 H). − ^{13}C NMR (125 MHz): δ = 135.1 (Cq), 131.9 (Cq), 45.5 (CH), 39.6 (CH), 33.3 (Cq), 13.7 (CH_3), 12.9 (CH_3), 11.3 (CH_3), 9.0 (CH_3), 5.6 (CH_2), 5.5 (CH_2). − MS (70 eV); *m*/*z* (%): 150 (33) [$M^{+\cdot}$], 135 (100). − HRMS, $C_{11}H_{18}$: calcd. 150.1409; found 150.1422.

Spiro[cyclopropane-1,3′-(4′-cholestene)] (11): Yield 357 mg (90%), solid, m.p. 94 °C. − IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1}, 2936, 1466, 1379. − ^{1}H NMR (500 MHz): δ = 4.67 (s, 1 H), 2.25−2.15 (m, 1 H), 2.05−0.80 (m, 39 H), 0.70 (s, 3 H), 0.52−0.30 (m, 4 H). − ^{13}C NMR (125 MHz): δ = 144.1 (Cq), 126.4 (CH), 56.3 (2 CH), 54.2 (CH), 42.5 (Cq), 40.1 (CH_2), 39.5 (CH_2), 37.3 (CH_2), 37.0 (Cq), 36.2 (CH_2), 36.0 (CH), 35.8 (CH), 33.2 (CH_2), 32.3 (CH_2), 30.0 (CH_2), 28.3 (CH_2), 28.0 (CH), 24.3 (CH_2), 23.9 (CH_2), 22.9 (CH_3), 22.6 (CH_3), 21.7 (CH_2), 19.1 (CH_3), 18.7 (CH_3), 18.7 (Cq), 15.1 (CH_2), 13.7 (CH_2), 12.0 (CH_3). − MS (70 eV); *m*/*z* (%): 397 (100) [$M^{+\cdot}$], 382 (17). − $C_{29}H_{48}$ (396.7): calcd. C 87.80, H 12.20; found C 87.56, H 12.51.

1,5,7,7-Tetramethylspiro[2.5]oct-4-ene (12): Yield 82 mg (50%, 1:1 mixture of isomers A and B), colourless oil. *Isomer A*: ^{1}H NMR (250 MHz): δ = 4.94 (s, 1 H), 1.90−1.70 (m, 2 H), 1.69 (s, 3 H), 1.65−1.57 (m, 1 H), 1.42 (d, *J* = 9.5 Hz, 1 H), 1.06 (d, *J* = 6.1 Hz,

3 H), 0.95 (s, 3 H), 0.93 (s, 3 H), 0.86−0.66 (m, 1 H), 0.62 (dd, J = 8.4, 4.2 Hz, 1 H), 0.15 (t, J = 4.6 Hz, 1 H). − ^{13}C NMR (62.5 MHz): δ = 133.2 (Cq), 123.7 (CH), 47.9 (CH_2), 44.8 (CH_2), 30.8 (Cq), 29.8 (CH_3), 27.4 (CH_3), 24.0 (CH_3), 21.5 (Cq), 20.6 (CH_2), 20.3 (CH), 14.5 (CH_3). − MS (70 eV); *m/z* (%): 164 (70) [$M^{+\cdot}$], 149 (100), 107 (69), 91 (45), 93 (59). *Isomer B*: ^{1}H NMR (250 MHz): δ = 4.63 (s, 1 H), 1.85−1.67 (m, 3 H), 1.64 (s, 3 H), 1.43 (d, J = 8.0 Hz, 1 H), 1.06 (d, J = 6.1 Hz, 3 H), 0.97 (s, 3 H), 0.96 (s, 3 H), 0.73−0.58 (m, 2 H), 0.18−0.12 (m, 1 H). − ^{13}C NMR (62.5 MHz): δ = 130.5 (Cq), 129.2 (CH), 44.5 (CH_2), 40.2 (CH_2), 30.5 (Cq), 29.3 (CH_3), 28.0 (CH_3), 23.6 (CH_3), 21.3 (Cq), 21.2 (CH_2), 18.2 (CH), 14.0 (CH_3). − MS (70 eV); *m/z* (%): 164 (70) [$M^{+\cdot}$], 149 (100), 107 (69). − HRMS, $C_{12}H_{20}$: calcd. 164.1565; found 164.1535.

(1-Vinylcyclopropyl)benzene[16] **(14):** Yield 102 mg (71%), yellow oil. − ^{1}H NMR (250 MHz): δ = 7.45−7.19 (m, 5 H), 5.74 (dd, J = 17.2, 10.3 Hz, 1 H), 4.92 (dd, J = 10.3, 1.1 Hz, 1 H), 4.60 (dd, J = 17.2, 1.1 Hz, 1 H), 1.15−1.07 (m, 2 H), 1.05−0.98 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 145.3 (CH), 143.0 (Cq), 129.8 (2 CH), 128.1 (2 CH), 126.3 (CH), 112.1 (CH_2), 18.7 (Cq), 14.7 (2 CH_2). − MS (70 eV); *m/z* (%): 144 (79) [$M^{+\cdot}$], 129 (94), 115 (100).

1-Nonyl-1-vinylcyclopropane (16): Yield 78 mg (40%), colourless oil. − IR (film): $\tilde{\nu}$ = 3073 cm^{-1}, 2922, 2847, 1454. − ^{1}H NMR (250 MHz): δ = 5.65−5.52 (m, 1 H), 4.95−4.85 (m, 2 H), 1.35−1.15 (m, 16 H), 0.89 (t, J = 7.3 Hz, 3 H), 0.59−0.50 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 144.1 (CH), 110.3 (CH_2), 36.0 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 14.0 (2 CH_2). − MS (70 eV); *m/z* (%): 194 (1) [$M^{+\cdot}$], 67 (100). − HRMS, $C_{14}H_{26}$: calcd. 194.2035; found 194.2018.

2-(1-Methylcyclopropyl)naphthalene (18): Yield 109 mg (64%), colourless oil. − IR (film): $\tilde{\nu}$ = 3078 cm^{-1}, 3054, 2949, 1634, 1601, 1508, 1458, 1426. − ^{1}H NMR (250 MHz): δ = 7.83−7.75 (m, 4 H), 7.50−7.35 (m, 3 H), 1.55 (s, 3 H), 1.05−1.00 (m, 2 H), 0.87−0.81 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 144.5 (Cq), 133.5 (Cq), 131.8 (Cq), 127.8 (CH), 127.5 (2 CH), 125.9 (CH), 125.6 (CH), 125.1 (CH), 124.9 (CH), 25.7 (CH_3), 20.0 (Cq), 15.5 (2 CH_2). − MS (70 eV); *m/z* (%): 182 (38) [$M^{+\cdot}$], 167 (100), 152 (45). − $C_{14}H_{14}$ (182.3): calcd. C 92.26, H 7.74; found C 92.20, H 7.96.

1-(4-Methoxyphenyl)bicyclopropane (20): Yield 131 mg (70%), colourless oil. − IR (film): $\tilde{\nu}$ = 3082 cm^{-1}, 2999, 1512, 1244. − ^{1}H NMR (250 MHz): δ = 7.29 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 3.80 (s, 3 H), 1.29−1.17 (m, 1 H), 0.71−0.56 (m, 4 H), 0.45−0.36 (m, 2 H), 0.36−0.07 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 157.7 (Cq), 138.8 (Cq), 129.0 (2 CH), 113.5 (2 CH), 55.2 (CH_3), 24.6 (Cq), 17.6 (CH), 11.2 (2 CH_2), 2.7 (2 CH_2). − MS (70 eV); *m/z* (%): 188 (64) [$M^{+\cdot}$], 157 (65), 129 (75), 115 (100). $C_{13}H_{16}O$ (188.3): calcd. C 82.94, H 8.57; found C 83.29, H 8.12.

1-Methyl-1-nonylcyclopropane (22): Yield 75 mg (42%), colourless oil. − IR (film): $\tilde{\nu}$ = 3069 cm^{-1}, 2938, 2853, 1462, 1379. − ^{1}H NMR (250 MHz): δ = 1.38−1.13 (m, 16 H), 1.01 (s, 3 H), 0.88 (t, J = 7.0 Hz, 3 H), 0.22−0.18 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 31.9 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 27.0 (CH_2), 22.8 (CH_3), 22.7 (CH_2), 15.3 (Cq), 14.1 (CH_3), 12.9 (2 CH_2). − MS (70 eV); *m/z* (%): 182 (0.03) [$M^{+\cdot}$], 70 (100), 56 (49). − HRMS, $C_{13}H_{26}$: calcd. 182.2035; found 182.2041.

Spiro[cyclopropane-1,3′-cholestane] (24): Yield 143 mg (36%), solid, m.p. 95 °C. − IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1}, 2936, 2847, 1466, 1379. − ^{1}H NMR (500 MHz): δ = 1.98 (dt, J = 12.6, 3.2 Hz, 1 H), 1.92 (td, J = 13.7, 3.8 Hz, 1 H), 1.87−1.77 (m, 1 H), 1.74 (t, J = 12.6 Hz, 1 H), 1.68−1.61 (m, 2 H), 1.61−1.49 (m, 3 H), 1.41−0.96 (m, 18 H), 0.94−0.84 (m, 1 H), 0.92 (d, J = 6.6 Hz, 3 H), 0.89 (d, J = 2.4 Hz, 3 H), 0.87 (d, J = 2.4 Hz, 3 H), 0.82 (s, 3 H), 0.76−0.68 (m, 1 H), 0.67 (s, 3 H), 0.66−0.61 (m, 1 H), 0.39 (dt, J = 12.6, 2.3 Hz, 1 H), 0.27−0.18 (m, 2 H), 0.17−0.12 (m, 2 H). − ^{13}C NMR (125 MHz): δ = 56.6 (CH), 56.3 (CH), 54.5 (CH), 45.7 (CH), 42.6 (Cq), 40.1 (CH_2), 39.5 (CH_2), 38.5 (CH_2), 37.6 (CH_2), 36.2 (CH_2), 35.9 (Cq), 35.8 (CH), 35.6 (CH), 32.1 (CH_2), 31.5 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 28.0 (CH), 24.2 (CH_2), 23.7 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 21.0 (CH_2), 19.0 (Cq), 18.7 (CH_3), 13.4 (CH_2), 12.1 (CH_3), 11.8 (CH_3), 11.2 (CH_2). − MS (70 eV); *m/z* (%): 398 (88) [$M^{+\cdot}$], 383 (60), 243 (100). − HRMS, $C_{29}H_{50}$: calcd. 398.3912; found 398.3901.

(*E*)-β-Cyclopropylstyrene[17] **(26):** Yield 109 mg (75%), colourless oil. − ^{1}H NMR (250 MHz): δ = 7.40−7.15 (m, 5 H), 6.50 (d, J = 16.0 Hz, 1 H), 5.75 (dd, J = 16.0, 9.1 Hz, 1 H), 1.67−1.52 (m, 1 H), 0.84 (dq, J = 8.4, 4.2 Hz, 2 H), 0.57−0.50 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 137.7 (Cq), 134.9 (CH), 128.4 (2 CH), 127.3 (CH), 126.5 (CH), 125.5 (2 CH), 14.5 (CH), 7.2 (2 CH_2). − MS (70 eV); *m/z* (%): 144 (50) [$M^{+\cdot}$], 129 (100), 128 (59). − HRMS, $C_{11}H_{12}$: calcd. 144.0939; found 144.0931.

(2,6-Dimethyl-1,5-heptadienyl)cyclopropane (28): Yield 113 mg (71%), mixture of isomers, colourless oil. − IR (film): $\tilde{\nu}$ = 3081 cm^{-1}, 2957, 2916, 2853, 1454, 1379, 1254. − ^{1}H NMR (500 MHz): δ = 5.20−5.15 (m, 1 H), 5.12−5.07 (m, 1 H), 4.55 (d, J = 9.2 Hz, 2 H), 2.20−2.10 (m, 4 H), 2.10−2.03 (m, 2 H), 2.02−1.93 (m, 2 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.69 (s, 6 H), 1.63 (s, 3 H), 1.61 (s, 3 H), 1.50−1.40 (m, 2 H), 0.71−0.62 (m, 4 H), 0.32−0.22 (m, 4 H). − ^{13}C NMR (125 MHz): δ = 134.3 (Cq), 134.0 (Cq), 131.5 (Cq), 131.3 (Cq), 129.3 (CH), 128.4 (CH), 124.4 (CH), 124.3 (CH), 39.6 (CH_2), 32.5 (CH_2), 26.8 (CH_2), 26.7 (CH_2), 25.7 (2 CH_3), 23.3 (CH_3), 17.7 (2 CH_3), 16.5 (CH_3), 9.9 (CH), 9.8 (CH), 6.6 (2 CH_2), 6.5 (2 CH_2). − MS (70 eV); *m/z* (%): 164 (4) [$M^{+\cdot}$], 95 (100), 67 (69). − HRMS, $C_{12}H_{20}$: calcd. 164.1565; found 164.1543.

1-Cyclopropyl-4-methoxybenzene[18] **(30):** Yield 130 mg (88%), colourless oil. − ^{1}H NMR (250 MHz): δ = 7.03 (d, J = 8.8 Hz, 2 H), 6.82 (d, J = 8.8 Hz, 2 H), 3.80 (s, 3 H), 1.94−1.80 (m, 1 H), 0.97−0.85 (m, 2 H), 0.70−0.58 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 157.5 (Cq), 135.8 (Cq), 126.8 (2 CH), 113.7 (2 CH), 55.2 (CH_3), 14.5 (Cq), 8.5 (2 CH_2).

2-Cyclopropylnaphthalene[19] **(32):** Yield 104 mg (58%), solid, m.p. 34 °C. − ^{1}H NMR (250 MHz): δ = 7.85−7.70 (m, 3 H), 7.55 (s, 1 H), 7.50−7.35 (m, 2 H), 7.25−7.16 (m, 1 H), 2.20−2.15 (m, 1 H), 1.10−1.01 (m, 2 H), 0.87−0.80 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 141.4 (Cq), 133.6 (Cq), 131.9 (Cq), 127.8 (CH), 127.6 (CH), 127.2 (CH), 125.9 (CH), 124.8 (CH), 124.6 (CH), 123.7 (CH), 15.6 (CH), 9.1 (2 CH_2). − MS (70 eV); *m/z* (%): 168 (80) [$M^{+\cdot}$], 167 (100), 165 (42), 153 (46), 152 (49). − $C_{13}H_{12}$ (168.2): calcd. C 92.81, H 7.19; found C 93.18, H 7.71.

1-Heptadecylcyclopropane (34): Yield 39 mg (21%), colourless oil. − IR (film): $\tilde{\nu}$ = 3063 cm^{-1}, 2916, 2832, 1454, 1369, 1001. − ^{1}H NMR (250 MHz): δ = 1.35−1.17 (m, 33 H), 0.93−0.82 (m, 7 H). − ^{13}C NMR (62.5 MHz): δ = 35.6 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (8 CH_2), 29.4 (CH_2), 28.6 (CH_2), 26.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 11.7 (2 CH_2), 10.7 (CH). − MS (70 eV); *m/z* (%): 111 (16), 97 (33), 84 (100), 70 (77). $C_{20}H_{40}$ (280.5): calcd. C 85.63, H 14.37; found C 85.81, H 14.82.

(*Z*)-β-Bromo-β-cyclopropylstyrene (36): Yield 125 mg (56%), yellow oil. − IR (film): $\tilde{\nu}$ = 3086 cm^{-1}, 3058, 3011, 2926, 1630, 1495,

1437, 743, 692. − ^{1}H NMR (250 MHz): δ = 7.63−7.55 (m, 2 H), 7.45−7.22 (m, 3 H), 6.86 (s, 1 H), 1.98−1.85 (m, 1 H), 0.95−0.79 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 136.2 (Cq), 129.8 (Cq), 128.9 (2 CH), 128.0 (2 CH), 127.4 (CH), 126.0 (CH), 22.1 (CH), 7.4 (2 CH_2). − MS (70 eV); *m/z* (%): 224 (2) [M + 1], 222 (2) [M − 1], 142 (54), 141 (100), 115 (65). − HRMS, $C_{11}H_{11}Br$: calcd. 222.0044; found 222.0020.

Ethyl 4-Ethyl-5-methylspiro[2.5]oct-4-ene-6-carboxylate (38): Yield 160 mg (72%), yellow oil. − IR (film): $\tilde{\nu}$ = 3073 cm^{-1}, 2957, 2874, 1730, 1454, 1369, 1304, 1244, 1154, 1035, 735. − ^{1}H NMR (500 MHz): δ = 4.15 (q, *J* = 7.3 Hz, 2 H), 3.07 (t, *J* = 6.1 Hz, 1 H), 1.94 (q, *J* = 5.7 Hz, 2 H), 1.69−1.60 (m, 1 H), 1.67−1.55 (m, 2 H), 1.65 (s, 3 H), 1.30−1.23 (m, 1 H), 1.26 (t, *J* = 6.9 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H), 0.80−0.65 (m, 2 H), 0.48−0.30 (m, 2 H). − ^{13}C NMR (125 MHz): δ = 175.4 (Cq), 137.8 (Cq), 123.3 (Cq), 60.2 (CH_2), 48.2 (CH), 33.3 (CH_2), 26.3 (CH_2), 19.4 (CH_2), 19.1 (Cq), 18.0 (CH_3), 14.2 (CH_3), 13.7 (CH_3), 12.3 (CH_2), 12.0 (CH_2). − MS (70 eV); *m/z* (%): 222 (12) [M$^+$], 149 (100), 131 (42), 93 (43), 91 (43). − HRMS, $C_{14}H_{22}O_2$: calcd. 222.1620; found 222.1598.

***N*-Benzyl-*N*-methyl-3-(1-phenylcyclopropyl)propionamide (40):** Yield 202 mg (69%, mixture of rotamers), yellow oil. − ^{1}H NMR (250 MHz): δ = 7.40−7.00 (m, 10 H), 4.55, 4.37 (2s, 2 H), 2.91, 2.78 (2s, 3 H), 2.40−2.28 (m, 2 H), 2.02−1.90 (m, 2 H), 0.90−0.68 (m, 4 H). − ^{13}C NMR (62.5 MHz): δ = 173.3 (Cq), 172.8 (Cq), 144.4 (Cq), 137.4 (Cq), 136.7 (Cq), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.9 CH), 127.4 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 125.9 (CH), 53.3 (CH_2), 50.6 (CH_2), 35.8 (CH_2), 35.5 (CH_2), 34.6 (CH_3), 33.9 (CH_3), 31.3 (CH_2), 30.9 (CH_2), 25.2 (Cq), 25.0 (Cq), 13.2 (CH_2), 13.1 (CH_2). − MS (70 eV); *m/z* (%): 293 (11) [M$^+$], 91 (100), 65 (13). − HRMS, $C_{20}H_{23}NO$: calcd. 293.1780, found 293.1804.

Spiro[cyclopropane-1,6′-(9′-methyl-Δ$^{5'(10')}$-1′-octalone)] (44): Yield 105 mg (55%), yellow oil. − IR (film): $\tilde{\nu}$ = 3073 cm^{-1}, 2936, 2860, 1705. − ^{1}H NMR (500 MHz): δ = 4.83 (s, 1 H), 2.63 (td, *J* = 14.6, 6.3 Hz, 1 H), 2.52 (td, *J* = 13.5, 3.9 Hz, 1 H), 2.37−2.31 (m, 1 H), 2.18−2.12 (m, 1 H), 2.00 (qd, *J* = 13.1, 3.1 Hz, 1 H), 1.99−1.94 (m, 1 H), 1.79 (td, *J* = 13.2, 2.1 Hz, 1 H), 1.68 (ddd, *J* = 13.4, 5.2, 3.1 Hz, 1 H), 1.57 (qt, *J* = 13.3, 4.6 Hz, 1 H), 1.31 (s, 3 H), 1.11 (m, 1 H), 0.57−0.41 (m, 4 H). − ^{13}C NMR (125 MHz): δ = 214.8 (Cq), 139.0 (Cq), 130.7 (CH), 50.1 (Cq), 38.4 (CH_2), 30.9 (CH_2), 30.5 (CH_2), 29.2 (CH_2), 25.6 (CH_2), 24.9 (CH_3), 18.4 (Cq), 15.1 (CH_2), 13.8 (CH_2). − MS (70 eV); *m/z* (%): 190 (31) [M$^+$], 147 (76), 133 (63), 119 (75), 105 (100). − HRMS, $C_{13}H_{18}O$: calcd. 190.1358; found 190.1335.

Spiro[cyclopropane-1,3′(4′-pregnen-20′-one)] (46): From progesterone: yield 140 mg (43%), from **48**: yield 228 mg (70%), solid, m.p. 125 °C. − IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2922, 2847, 1705. − ^{1}H NMR (500 MHz): δ = 4.66 (s, 1 H), 2.52 (t, *J* = 8.9 Hz, 1 H), 2.26−2.12 (m, 3 H), 2.12 (s, 3 H), 2.05−1.90 (m, 2 H), 1.77−1.58 (m, 5 H), 1.51−1.35 (m, 4 H), 1.27−1.10 (m, 2 H), 1.04 (s, 3 H), 0.98−0.84 (m, 3 H), 0.64 (s, 3 H), 0.54−0.51 (m, 2 H), 0.46−0.40 (m, 2 H). − ^{13}C NMR (125 MHz): δ = 209.7 (Cq), 143.7 (Cq), 126.7 (CH), 63.8 (CH), 56.4 (CH), 54.0 (CH), 44.2 (Cq), 39.0 (CH_2), 37.2 (CH_2), 37.0 (Cq), 35.9 (CH), 33.0 (CH_2), 32.1 (CH_2), 31.5 (CH_3), 29.8 (CH_2), 24.5 (CH_2), 22.7 (CH_2), 21.6 (CH_2), 19.1 (CH_3), 18.6 (Cq), 15.0 (CH_2), 13.7 (CH_2), 13.3 (CH_3). − MS (70 eV); *m/z* (%): 326 (100) [M$^+$], 325 (88). − HRMS, $C_{23}H_{34}O$: calcd. 326.2610; found 326.2597.

17-(1-Methylcyclopropyl)-4-androsten-3-one[20] **(47):** Yield 59 mg (18%), solid, m.p. 153 °C. − IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1}, 2936, 2847, 1666. − ^{1}H NMR (500 MHz): δ = 5.73 (s, 1 H), 2.46−2.23 (m, 4 H), 2.14−1.99 (m, 2 H), 1.87−1.80 (m, 1 H), 1.75−1.40 (m, 7 H), 1.23−0.85 (m, 6 H), 1.19 (s, 3 H), 1.07 (s, 3 H), 0.77 (s, 3 H), 0.47 (ddd, *J* = 9.4, 5.3, 4.5 Hz, 1 H), 0.27 (ddd, *J* = 9.4, 5.2, 4.2 Hz, 1 H), 0.18 (ddd, *J* = 9.2, 5.2, 4.5 Hz, 1 H), 0.01 (ddd, *J* = 9.2, 5.3, 4.2 Hz, 1 H) − ^{13}C NMR (125 MHz): δ = 199.7 (Cq), 171.7 (Cq), 123.7 (CH), 55.8 (CH), 55.6 (CH), 53.8 (CH), 43.9 (Cq), 39.4 (CH_2), 38.6 (Cq), 35.7 (CH_2), 35.3 (CH), 34.0 (CH_2), 33.9 (CH_2), 32.0 (CH_2), 25.2 (CH_3), 24.1 (CH_2), 23.8 (CH_2), 20.8 (CH_2), 17.4 (CH_3), 14.6 (Cq), 13.4 (CH_3), 10.9 (CH_2), 10.8 (CH_2). − MS (70 eV); *m/z* (%): 327 (41) [M$^+$], 298 (42), 269 (50), 124 (100). − HRMS, $C_{23}H_{34}O$: calcd. 326.2610; found 326.2587.

20-Ethylenedioxy-4-pregnen-3-one[21] **(48):** Yield 179 mg (50%), solid, m.p. 190 °C. − IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1}, 2886, 1680, 1229, 1053. − ^{1}H NMR (500 MHz): δ = 5.71 (s, 1 H), 4.02−3.91 (m, 2 H), 3.91−3.83 (m, 2 H), 2.45−2.25 (m, 4 H), 2.10−1.97 (m, 2 H), 1.88−1.60 (m, 6 H), 1.58−1.35 (m, 3 H), 1.28 (s, 3 H), 1.21−1.16 (m, 2 H), 1.18 (s, 3 H), 1.07−0.87 (m, 3 H), 0.80 (s, 3 H). − ^{13}C NMR (125 MHz): δ = 199.6 (Cq), 171.5 (Cq), 123.7 (CH), 111.8 (Cq), 65.2 (CH_2), 63.2 (CH_2), 58.1 (CH), 55.7 (CH), 53.7 (CH), 41.8 (Cq), 39.2 (CH_2), 38.6 (Cq), 35.6 (CH_2), 35.0 (CH), 33.9 (CH_2), 32.9 (CH_2), 31.9 (CH_2), 24.5 (CH_3), 23.7 (CH_2), 22.9 (CH_2), 20.8 (CH_2), 17.3 (CH_3), 12.9 (CH_3). − MS (70 eV); *m/z* (%): 359 (37) [M + 1], 343 (100). − $C_{23}H_{34}O_3$ (358.5): calcd. C 77.05, H 9.63; found C 77.03, H 9.56.

1-Heptadecyl-1-cyclopropanol: The general procedure employing Lewis acid was applied to a mixture of isophorone (1 mmol) and methyl stearate (1 mmol) to give **7** (63 mg, 42%) and the title cyclopropanol: yield 53 mg (18%), solid, m.p. 56 °C. − IR (KBr): $\tilde{\nu}$ = 3337 cm^{-1}, 3248, 3086, 2922, 2847, 1466. − ^{1}H NMR (250 MHz): δ = 1.60−1.45 (m, 3 H), 1.40−1.15 (m, 30 H), 0.88 (t, *J* = 6.5 Hz, 3 H), 0.77−0.71 (m, 2 H), 0.47−0.42 (m, 2 H). − ^{13}C NMR (62.5 MHz): δ = 55.9 (Cq), 38.3 (CH_2), 31.9 (CH_2), 29.7 (11 CH_2), 25.9 (CH_2), 29.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 13.5 (2 CH_2). − MS (70 eV); *m/z* (%): 296 (10) [M$^+$], 267 (100), 109 (44). − HRMS, $C_{20}H_{40}O$: calcd. 296.3079; found 296.3107.

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Received May 16, 2000
[O00246]