A Facile Synthesis of 1,2-Divinylcycloalkanols and Their Behavior in the Oxy-Cope Rearrangement[1)]

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The reaction of 2-chlorocycloalkanones with vinylmagnesium chloride gives 1,2-divinylcycloalkanols. Divinylation proceeds *via* a rearrangement of initially formed 2-chloro-1-vinylcycloalkanols to 2-vinylcycloalkanones followed by further vinylation of 2-vinylcycloalkanones. Thermal sigmatropic rearrangement of 1,2-divinylcycloalkanols gives 5-cycloalken-1-ones in good yields. The influence of the size of rings on the reaction pathways is discussed.

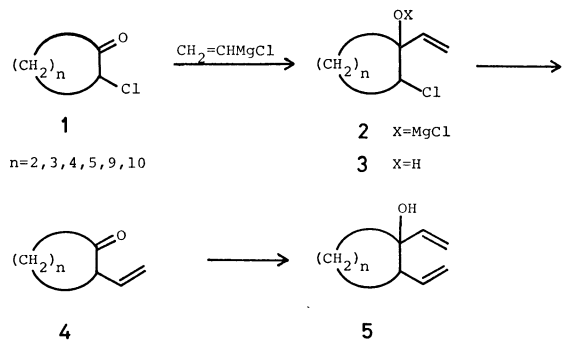
The oxy-Cope rearrangements are powerful reactions for the preparation of α,ε-unsaturated carbonyl compounds and α,δ-dicarbonyl derivatives.[2)] Marvell and Whally extended this utility to the formation of tenmenbered rings from *trans*- and *cis*-1,2-divinylcyclohexanols.[3)] Although good yields can be obtained in these reactions, the preparation of 1,2-divinylcyclohexanols requires multistep reactions, *i.e.*, vinylation of cyclohexene oxide with vinyllithium and oxidation of the resulting 2-vinylcyclohexanol with chromium trioxide followed by vinylation of 2-vinylcyclohexanone with vinylmagnesium bromide. We wish to report on the one-step synthesis of 1,2-divinylcycloalkanols and their behavior in the oxy-Cope rearrangement. The influence of the size of rings on the reaction pathways is also discussed.

Results and Discussion

Divinylation of 2-Chlorocycloalkanones. The reaction of 2-chlorocycloalkanones **1** with vinylmagnesium chloride in tetrahydrofuran (THF)[4)] gives 1,2-divinylcycloalkanols **5**. Divinylation was carried out in the presence of more than 2 molar equiv of vinylmagnesium chloride at temperatures above 50 °C. The results are summarized in Table 1.

The results suggest that the yields of 1,2-divinylcycloalkanols **5** are markedly influenced by the size of rings, decreasing in the order: n=4>5>10>3>9>2. The reaction of 2-chlorocyclobutanone **1a** showed an exceptional trend, affording no detectable amount of 1,2-divinylcyclobutanol **5a**.

Divinylation of 2-chlorocycloalkanones **1**, except for



Scheme 1.

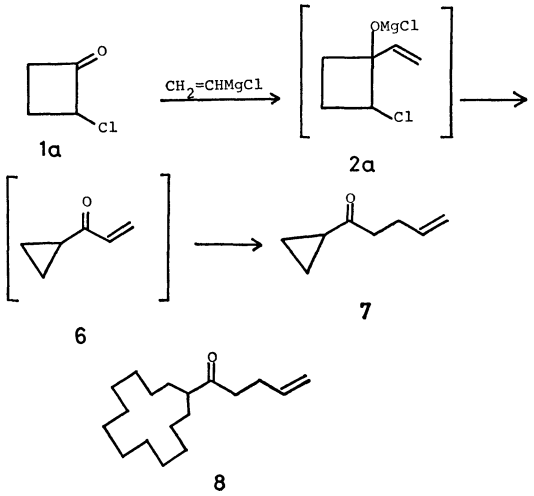
Table 1. Divinylation of 2-chlorocycloalkanones with vinylmagnesium chloride

	n	Molar ratio CH_2=CHMgCl/**1**	Temp/°C	Yield **5** (%)
1a	2	2.60	55	0
1b	3	2.32	55	31
1c	4	2.50	55	90
1d	5	2.52	55	75
1e	9	2.20	55	7
1f	10	2.20	55	53

the case of 2-chlorocyclobutanone **1a**, was found to proceed *via* the vinyl group rearrangement of the initially formed chlorohydrin derivatives **2**, followed by further vinylation of the resulting 2-vinylcycloalkanones **4**. The reaction pathways can be reasonably accounted for by the following observations. Treatment of 2-chlorocycloalkanones **1** with vinylmagnesium chloride in THF below room temperature predominantly affords chlorohydrins **3**.[5,6)] The direct attack of vinylmagnesium chloride on chlorine atom is a minor reaction pathway.[7)] For example, when 2-chlorocyclododecanone **1f** was treated with 1.15 molar equiv of vinylmagnesium chloride in THF at 0 °C, 2-vinylcyclododecanone **4f** was obtained in less than 1.6% yield, whereas 2-chloro-1-vinylcyclododecanol **3f** was obtained in 87—94% yield.

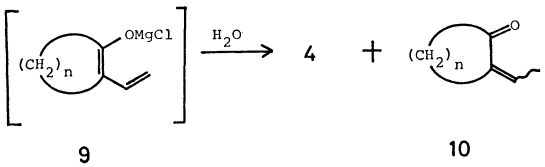
1,2-Migration of the vinyl group in chlorohydrins **3** takes place smoothly to afford 2-vinylcycloalkanones **4** when the magnesium salts of the chlorohydrins **3** (n= 3, 4, 5, 9, 10) are heated[5-9)] in a solution above 50 °C. On the other hand, the reaction of 2-chlorocyclobutanone **1a** with vinylmagnesium chloride predominantly affords 1-cyclopropyl-4-penten-1-one **7**. Formation of **7** can be rationalized by assuming that the reaction proceeds *via* the ring contraction of the chlorohydrin derivative **2** (n=2) in place of the vinyl group rearrangement, followed by the conjugate addition of vinylmagnesium chloride to the resulting 1-cyclopropyl-2-propen-1-one **6**.[10)] In the reaction of 2-chlorocycloalkanones **1** (n=3, 4, 5, 9,10) the ring contraction is a minor pathway. For example, 2-chlorocyclododecanone **1f** upon treatment with vinylmagnesium chloride at 55 °C gave 1-cycloundecyl-4-penten-1-one **8** only in 2% yield.

2-Vinylcycloalkanones **4** were easily converted into 1,2-divinylcycloalkanols **5** with vinylmagnesium chloride



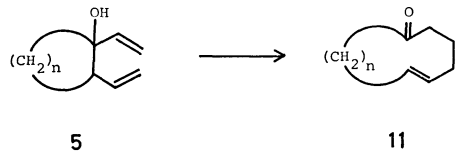
Scheme 2.

in THF at 0 °C. The major side reaction in the vinylation of **4** is the formation of enolates **9**[11] which upon hydrolysis lead to the recovery of **4** as well as the formation of 2-ethylidenecycloalkanones **10.**



Scheme 3.

The Oxy-Cope Rearrangement of 1,2-Divinylcycloalkanols. Thermal [3,3] sigmatropic rearrangement of 1,2-divinylcycloalkanols **5** at 165—220 °C gave 5-cycloalken-1-ones **11.** The rearrangement was carried out by using a mixture of *trans-* and *cis-*1,2-divinylcycloalkanols prepared by the direct divinylation of 2-chlorocycloalkanones **1.** The results are summarized in Table 2. When 1,2-divinylcyclohexanol **5c** was used, the highest yield (82%) was obtained. The yields of **11** decreased



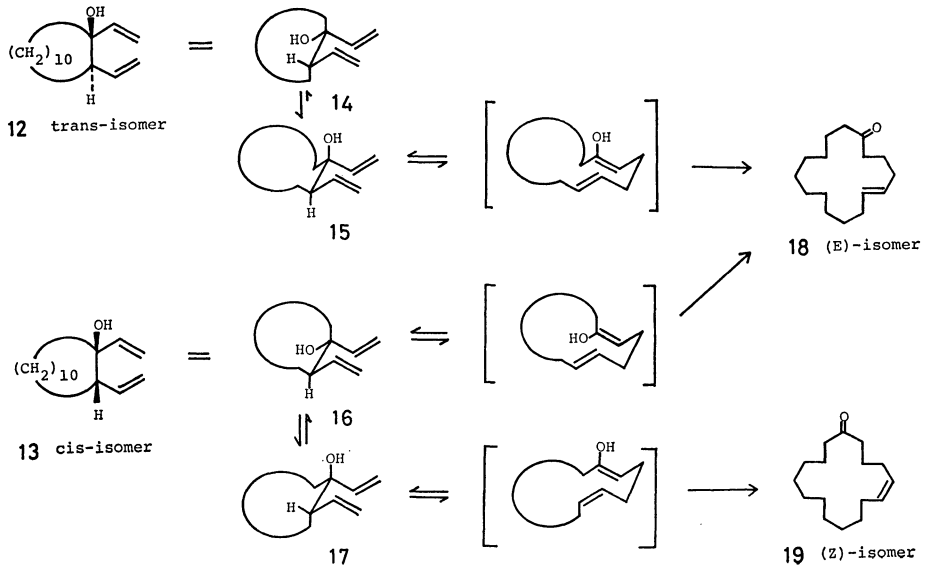
Scheme 4.

Table 2. Thermal [3,3] sigmatropic rearrangement of 1,2-divinylcycloalkanols

	n	Temp/°C	Time/h	Yield **11** (%)
5b	3	200	4	60
5c	4	220	2	82
5d	5	220	2	80
5e	9	180	2	74
5f	10	165	6	77

in the order: n=4>5>10>9>3.

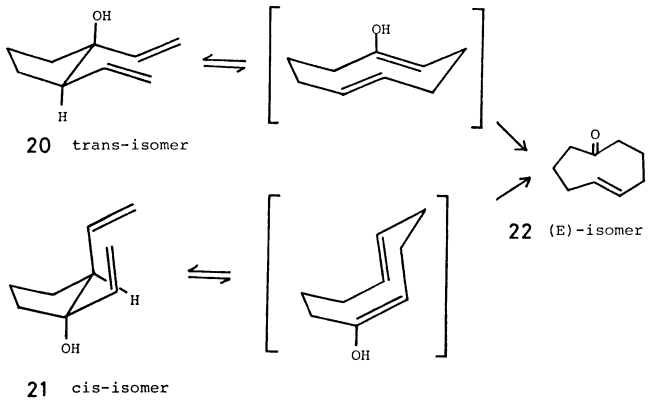
Marvell and Whally examined the thermal rearrangement of *trans-* and *cis-*1,2-divinylcyclohexanols to 5-cyclodecen-1-one **11c** in detail.[3] We have examined the thermal rearrangement of *trans-***12** and *cis-*1,2-divinylcyclododecanols **13,** and *trans-***20** and *cis-*1,2-divinylcyclopentanols **21** in order to clarify the influence of the size of rings on the oxy-Cope rearrangement. Divinylation of 2-chlorocyclododecanone **1f** afforded a 40 : 60 ratio of *trans-***12** and *cis-*1,2-divinylcyclododecanols **13.** When the minor isomer was heated at 180 °C for 3 h, the single product, (*E*)-5-cyclohexadecen-1-one **18** was obtained in 92% yield. The major isomer, under the same conditions, provided a mixture containing (*E*)-**18** and (*Z*)-5-cyclohexadecen-1-ones **19** in 24: 76 ratio in 67% yield. Infrared spectroscopy was used to distinguish (*E*)- (970 cm^{-1}) **18** from (*Z*)-5-cyclohexadecen-1-ones (720 cm^{-1}) **19.** Assuming that the rearrangement involves a concerted stereospecific Cope reaction *via* a chair-like transition state (**15, 16,** and **17**),[12] which minimizes 1,3-pseudo-diaxial interactions, the major isomer can be assigned to *cis-*1,2-



Scheme 5.

divinylcyclododecanol **13**. The stereochemical results are similar to those of 1,2-divinylcyclohexanols.[3]

Divinylation of 2-chlorocyclopentanone **1b** afforded an 81: 19 ratio of *trans*- **20** and *cis*-1,2-divinylcyclopentanols **21**. The major isomer was assigned to *trans*-1,2-divinylcyclopentanol **20** on the basis of the predominance of *trans* products in the addition of the Grignard reagents to 2-alkylcyclopentanones.[13] The thermal rearrangement of both *trans*- **20** and *cis*-1,2-divinylcyclopentanols **21** provided the single product (*E*)-5-cyclononen-1-one **22**,[14] in 46 and 72% yields, respectively, no detectable amount of (*Z*)-5-cyclononen-1-one being obtained. The stereochemistry of the product can be rationalized by assuming that chair-like transition geometries (**20** and **21**) are involved in the rearrangement of *trans*- and *cis*-1,2-divinylcyclopentanols.[15]



Scheme 6.

Experimental

Melting and boiling points are uncorrected. Gas-liquid chromatography (GLPC) analyses were performed on a Shimadzu 3BT instrument using 10% Silicone OV-17 or 5% PEG-20M coated on Chromosorb WHP (80—100 mesh) packed in glass columns (1.2 m). The following spectrometers were used: IR, Hitachi 215; NMR, Varian XL-100 or JEOL FX-100 (TMS as an internal standard); mass spectra, Hitachi RMU-7M or RMS-4. Silica gel (Merck, 70—230 mesh) was used for column chromatography. Unless otherwise stated, 2-chloro-1-vinylcycloalkanols **3**, 1,2-divinylcycloalkanols **5**, and 5-cycloalken-1-ones **11** consist of *trans*- and *cis*-isomers, or (*E*)- and (*Z*)-isomers.

2-Chlorocycloalkanones (1). 2-Chlorocycloalkanones **1** were prepared by the chlorination of cycloalkanones.[16-18]

Chlorohydrins (3). *Typical Procedure*: A solution of 2-chlorocycloundecanone **1e** (16.0 g, 79.0 mmol) in THF (20 ml) and a solution of vinylmagnesium chloride in THF (1.73 mol/l, 54.8 ml, 94.8 mmol) were added dropwise to THF (183 ml) at 0 °C during a period of 1 h. The mixture was stirred at 0 °C for 1.5 h, poured into an aqueous ammonium chloride solution and extracted with hexane. The hexane extracts were washed with water, dried over anhydrous sodium sulfate and concentrated to give 16.95 g of oil. GLPC analysis showed two major peaks due to 2-chloro-1-vinylcycloundecanol **3e** (69.3%). The oil was chromatographed on silica gel (benzene) to give a mixture of *trans*- and *cis*-2-chloro-1-vinylcycloundecanols (7.18 g, 39%). **3e**: bp 112—113 °C/0.6 Torr, mp 37—40 °C; IR (neat) 3570, 3080, 1643, 1140, 988, 922 cm^{-1}; NMR (CCl_4) δ 1.1—2.4 (m, 18H), 2.02 (s, 1H), 4.18 (dd, J=3 and 8 Hz, 1H), 5.10 (dd, J=2 and 11 Hz, 1H), 5.30 (dd, J=2 and 17 Hz, 1H), 5.96 (dd, J=11 and 17 Hz, 1H); MS *m/e* 232, 230 (M^+). Found: C, 67.92; H, 10.06; Cl, 15.34%. Calcd for $C_{13}H_{23}OCl$: C, 67.66; H, 10.05; Cl, 15.36%.

2-Chloro-1-vinylcyclobutanol (3a): Bp 65—75 °C/21 Torr; IR (neat) 3445, 1638, 985, 925, 855 cm^{-1}; NMR (CCl_4) δ 1.7—2.7 (m, 5H), 4.16—4.38 (m, 1H), 4.98—5.46 (m, 2H), 5.85 (dd, J=10 and 16 Hz, 1H). MS *m/e* 134, 132 (M^+). Found: C, 54.49; H, 6.91; Cl, 26.64%. Calcd for C_6H_9OCl: C, 54.34; H, 6.79; Cl, 26.79%.

2-Chloro-1-vinylcyclododecanol (3f, trans-*Isomer)*: Mp 55—55.5 °C; IR (KBr) 3550, 1640, 1118, 988, 919, 758 cm^{-1}; NMR (CCl_4) δ 1.1—2.3 (m, 21H), 4.03 (d, J=8 Hz, 1H), 5.10 (dd, J=2 and 11 Hz, 1H), 5.29 (dd, J=2 and 17 Hz, 1H), 5.92 (dd, J=11 and 17 Hz, 1H); MS *m/e* 246, 244 (M^+). Found: C, 68.47; H, 10.07; Cl, 14.63%. Calcd for $C_{14}H_{25}OCl$: C, 68.69; H, 10.29; Cl, 14.48%. (*3e*, cis-*isomer*): mp 63—65 °C; IR (KBr) 3550, 1638, 994, 908, 768 cm^{-1}; NMR (CCl_4) δ 1.0—2.3 (m, 21H), 4.03 (d, J=8 Hz, 1H), 5.05 (dd, J=2 and 11 Hz, 1H), 5.27 (dd, J=2 and 17 Hz, 1H), 5.90 (dd, J=11 and 17 Hz, 1H); MS *m/e* 246, 244 (M^+). Found: C, 68.51; H, 10.08; Cl, 14.52%. Calcd for $C_{14}H_{25}OCl$: C, 68.69; H, 10.29; Cl, 14.48%.

2-Vinylcycloalkanones (4). *Typical Procedure*: A solution of 2-chloro-1-vinylcycloundecanol **3e** (6.99 g, 30.3 mmol) in benzene (98 ml) was added to a stirred solution of ethylmagnesium bromide in ether (1.87 mol/l, 15.1 ml, 28.3 mmol) at 0 °C during a period of 1 h. After being stirred at 0 °C for 10 min, the reaction mixture was heated at 70 °C for 30 min, cooled, poured into an aqueous ammonium chloride solution and extracted with benzene. The benxene extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled (bp 91—93 °C/0.5—0.6 Torr) to give 5.16 g of oil. GLPC analysis showed one major peak due to 2-vinylcycloundecanone **4e** (82.7%). The yield of **4e** was 74%. The oil was chromatographed on silica gel (benzene) to give pure **4e** (2.60 g). **4e**: bp 88—89 °C/0.5 Torr; mp 35—37 °C; IR (neat) 3080, 1720, 1635, 995, 915 cm^{-1}; NMR (CCl_4) δ 1.1—2.3 (m, 16H), 2.3—2.7 (m, 2H), 3.29 (t, J=9 Hz, 1H), 4.91—5.18 (m, 2H), 5.50—5.90 (m, 1H); MS *m/e* 194 (M^+). Found: C, 80.51; H, 11.56%. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41%.

2-Vinylcyclododecanone (4f): Bp 80—84 °C/0.2 Torr; n_D^{20}= 1.4943; IR (neat) 3080, 1712, 1638, 995, 915 cm^{-1}; NMR (CCl_4) δ 1.0—2.1 (m, 18H), 2.25—2.60 (m, 2H), 3.10—3.40 (m, 1H), 4.90—5.20 (m, 2H), 5.53—5.94 (m, 1H); MS *m/e* 208 (M^+). Found: C, 67.84; H, 10.20; N, 15.88%. Calcd for $C_{15}H_{27}ON_3$ (semicarbazone, mp 182—184 °C): C, 67.84; H, 10.27; N, 15.84%.

1,2-Divinylcycloalkanols (5). *Typical Procedure*: A solution of 2-vinylcycloundecanone **4e** (2.40 g, 12.4 mmol) in THF (10 ml) was added dropwise to a stirred solution of vinylmagnesium chloride in THF (1.00 mol/l, 23.2 ml, 23.2 mmol) at 0 °C during a period of 1 h. After being stirred at 0 °C for 1.5 h, the reaction mixture was poured into an aqueous ammonium chloride solution and extracted with hexane. The hexane extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled (oil bath 140 °C/0.5 Torr) to give 1.71 g of oil. GLPC analysis showed a peak due to 1,2-divinylcycloundecanol **5e** (23.5%). The yield of **5e** from **4e** was 14.6%. The oil was chromatographed on silica gel (benzene) to give pure **5e**. **5e**: IR (neat) 3470, 3070, 1638, 1175, 1125, 995, 915 cm^{-1}; NMR (CCl_4) δ 1.0—2.0 (m, 19H), 2.0—2.3 (t, J=4 Hz, 1H), 4.65—5.10 (m, 4H),

5.30—5.85 (m, 2H); Found: C, 80.99; H, 11.65%. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78%.

*1,2-Divinylcyclopentanol (**5b**, trans-Isomer)*: $n_D^{23}=1.4810$; IR (neat) 3500, 3080, 1648, 1000, 920 cm^{-1}; NMR (CCl_4) δ 1.5—2.0 (m, 7H), 2.10—2.45 (m, 1H), 4.80—5.24 (m, 4H), 5.42—5.90 (m, 2H). Found: C, 78.42; H, 10.19%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

*(**5b**, cis-Isomer)*: $n_D^{23}=1.4859$; IR (neat) 3430, 3080, 1645, 995, 918 cm^{-1}; NMR (CCl_4) δ 1.3—2.6 (m, 8H), 4.70—5.18 (m, 4H), 5.30—5.90 (m, 2H). Found: C, 77.71; H, 10.23%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.20%.

*1,2-Divinylcyclohexanols (**5c**, trans- and cis-Isomers)*: The IR and NMR spectra of **5c** were identical with those of authentic samples.[3]

*1,2-Divinylcyclododecanol (**5f**, trans-Isomer)*: Mp 51—52 °C; IR (KBr) 3400, 3060, 1638, 997, 980, 918, 906 cm^{-1}; NMR (CCl_4) δ 1.0—2.0 (m, 21H), 2.15 (t, $J=10$ Hz, 1H), 4.70—6.02 (m, 6H). Found: C, 81.59; H, 11.99%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

*(**5f**, cis-Isomer)*: Bp 122—123 °C/0.7 Torr; mp 15—16 °C; $n_D^{20}=1.5023$; IR (neat) 3540, 3060, 1638, 998, 920 cm^{-1}; NMR (CCl_4) δ 0.95—1.9 (m, 21H), 2.30 (t, $J=10$ Hz, 1H), 4.88—6.02 (m, 6H). Found: C, 81.51; H, 11.91%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

*Direct Divinylation of 2-Chlorocycloalkanones (**1**) with Vinylmagnesium chloride. Typical Procedure*: A solution of 2-chlorocycloundecanone **1e** (10.1 g, 50.0 mmol) in THF (12 ml) and a solution of vinylmagnesium chloride in THF (1.73 mol/l, 34.7 ml, 60.0 mmol) were added dropwise to THF (60 ml) at 0 °C during a period of 1 h. Stirring was continued at 0 °C for 1.5 h. After a solution of vinylmagnesium chloride in THF (1.73 mol/l, 28.9 ml, 50.0 mmol) had been added during a period of 10 min, the reaction mixture was heated at 55 °C for 15 h, poured into an aqueous ammonium chloride solution and extracted with benzene. The benzene extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled (bp 100—106 °C/0.5 Torr) to give 6.28 g of oil. GLPC analysis showed a peak due to 1,2-divinylcycloundecanol **5e** (12.9%). The yield of **5e** from **1e** was 7.3%.

*Thermal Rearrangement of 1,2-Divinylcycloalkanols (**5**).*

Typical Procedure: *trans*-1,2-Divinylcyclopentanol **20** (3.00 g, 16.7 mmol) was heated at 200 °C for 3 h. The reaction mixture was distilled (bp 61 °C/3 Torr) to give 1.47 g of oil. GLPC analysis showed one major peak (94.5%) due to (*E*)-5-cyclononen-1-one **22**. The yield was 46%. *cis*-1,2-Divinylcyclopentanol **21** (1.00 g, 5.55 mmol), under the same conditions, gave an oil (0.68 g) containing (*E*)-5-cyclononen-1-one **22** (94.6%) as a major product, the yield being 72%. The IR and NMR spectra of (*E*)-5-cyclononen-1-one **22** were identical with those of an authentic sample.[14]

*5-Cyclodecen-1-one [**11c**, (E)- and (Z)-Isomers]*: The IR and NMR spectra of **11c** were identical with those of authentic samples.[3]

*5-Cycloundecen-1-one (**11d**)*: Bp 74 °C/1 Torr; $n_D^{25}=1.4904$; IR (neat) 3025, 1718, 1625, 980, 762 cm^{-1}; NMR (CCl_4) δ 1.1—2.6 (m, 16H), 4.88—5.48 (m, 2H); MS *m/e* 166 (M^+). Found: C, 79.93; H, 10.93%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

*5-Cyclopentadecen-1-one (**11e**)*: Mp 28—29 °C; IR (Nujol) 3025, 1720, 970, 739 cm^{-1}; NMR (CCl_4) δ 1.1—2.5 (m, 24H), 5.18—5.34 (m, 2H); MS *m/e* 194 (M^+). Found: C, 81.35; H, 11.76%. Calcd for $C_{15}H_{26}O$: C, 81.01; H, 11.78%.

*5-Cyclohexadecen-1-one [**11f**, (E)-Isomer]*: BP 114 °C/0.1 Torr; mp 11—12.5 °C; $n_D^{20}=1.4883$; IR (neat) 3040, 2940, 2880, 1710, 970 cm^{-1}; NMR (CCl_4) δ 1.1—1.8 (m, 18H), 1.8—2.1 (m, 4H), 2.1—2.4 (m, 4H), 5.18—5.34 (m, 2H). Found: C, 81.27; H, 11.64%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

*5-Cyclohexadecen-1-one [**11f**, (Z)-Isomer]*: Bp 137 °C/0.5 Torr; mp 36—37 °C, IR (neat) 3040, 2940, 1710, 1460, 720 cm^{-1}; NMR (CCl_4) δ 1.1—1.8 (m, 18H), 1.8—2.1 (m, 4H), 2.2—2.4 (m, 4H), 5.18—5.36 (m, 2H). Found: C, 81.35; H, 11.75%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

*1-Cyclopropyl-4-penten-1-one (**7**)*. A solution of vinylmagnesium chloride in THF (1.73 mol/l, 120 ml, 208 mmol) was added to a stirred solution of 2-chlorocyclobutanone **1a** (8.34 g, 79.9 mmol) in THF (70 ml) at 0 °C during a period of 2 h. The mixture was heated at 55 °C for 20 h, poured into an aqueous ammonium chloride solution and extracted with ether. The ether extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled (bp 60—90 °C/20 Torr) to give 5.60 g of oil. The oil was chromatographed on silica gel to give pure **7**. **7**: IR (neat) 3075, 1705, 1642, 1085, 1000, 915 cm^{-1}; NMR (CCl_4) δ 0.5—1.1 (m, 4H), 1.7—2.0 (m, 1H), 2.14—2.44 (m, 2H), 2.44—2.70 (m, 2H), 4.82—5.16 (m, 1H); MS *m/e* 124 (M^+). Found: C, 77.02; H, 9.61%. Calcd for $C_8H_{11}O$: C, 77.37; H, 9.74%.

*1-Cycloundecyl-4-penten-1-one (**8**)*: Bp 116—118 °C/0.3 Torr; $n_D^{25}=1.4873$; IR (neat) 3070, 1710, 1640, 995, 910 cm^{-1}; NMR (CCl_4) δ 1.1—1.8 (m, 20H), 2.2—2.5 (m, 5H), 4.82—5.12 (m, 2H), 5.55—5.96 (m, 1H); MS *m/e* 236 (M^+). Found: C, 81.29; H, 11.93%. Calcd for $C_{16}H_{28}O$: C, 81.27; H, 11.82%.

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