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CYCLIZATION OF 1,5-HEXADIEN-3-OLS. OBTENTION OF CHLORO-OCTALINES, OCTALONES AND HEXAHYDRO-AZULENONES FROM ALLYL-PULEGOLS

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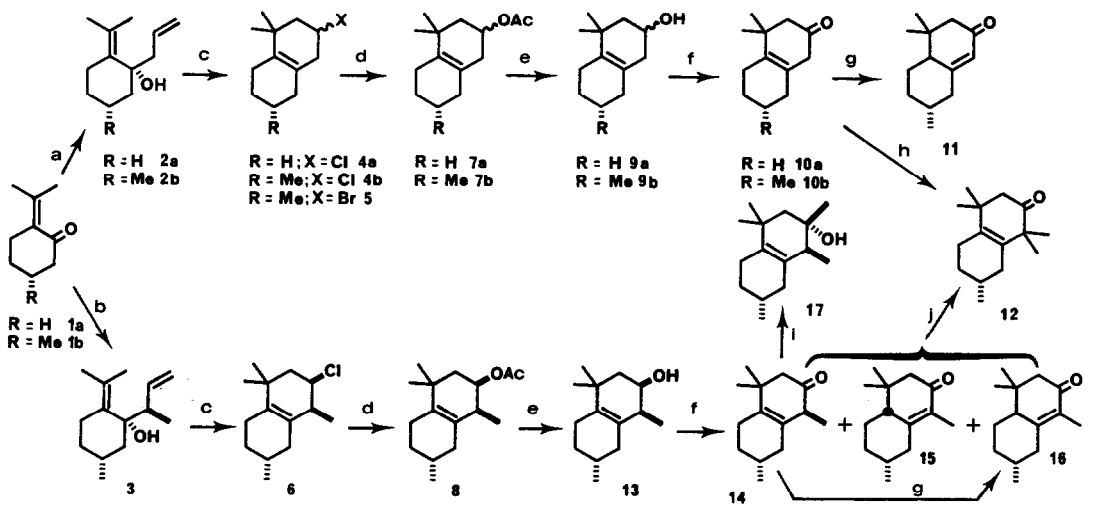
Summary : The $TiCl_4$ mediated cyclization of allyl-pulegols gives chlorooctalines (1,5-hexadien-3-ol system is cyclized into 4-chlorocyclohexene moiety). From chloro-octalines, octalones and hexahydro-azulenones are obtained respectively into three and two steps.

The biogenetic-like cyclization of polyolefins has been developed extensively and used for the construction of terpenoid systems.[1] The possibility of extending this concept to 1,5-hexadien-3-ol system is attractive for several reasons, not the least of which are the ready access to dienic alcohols (addition of allylmetals to enones)[2] as well as the favorable prospect for elaboration of residual functionnality after cyclization. Recently, we have reported an efficient cyclization of this type,[3] which affords direct entry to a decalin system of broad potential utility in terpene synthesis.



a : Allyl chloride and Mg; **b** : crotyl chloride and Mg; **c** : $TiCl_4$; **d** : $(AcO)_2Hg$, BF_3; **e** : $LiAlH_4$; **f** : CrO_3, H^+; **g** : standing or H^+; **h** : $LiNH_2$, MeI; **i** : MeMgI; **j** : LDA, MeI.

We have shown that allyl-Grignard reagents add stereospecifically to (+)-(R)-pulegone **1b** giving allyl-pulegols **2b** or **3**.[4]

The reaction of alcohol **2b** with a yellow precipitate of 0.5 equivalent of $TiCl_4$ in Et_2O gave 85 % yield of a 1:1 mixture of **4b** (2R) and **4b** (2S). The apparent lack of stereoselectivity results probably from little difference of the overcrowding of both faces. When the cyclization was carried out in the presence of $MgBr_2$ ($|Cl|:|Br^-| = 33$), we have observed the formation of **4b** and **5** (**4b**:**5** = 82:18). The relative importance of **5** could result from the better nucleophilic character of the bromide anion.[5]

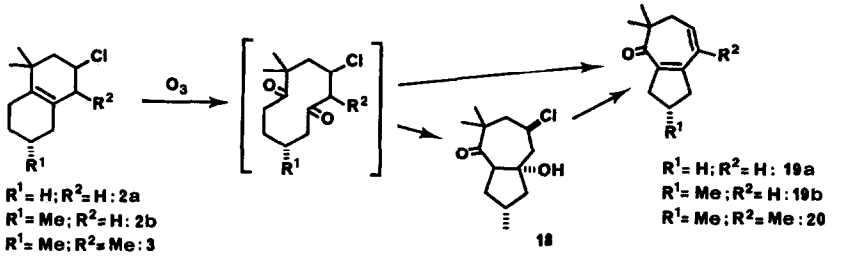
The $TiCl_4$ mediated cyclization of **3** gave 85-90 % yield of **6** as single product. The structure assignment was provided by ^1H NMR resonance of C(2)H. The vicinal coupling constant of 3.8 Hz observed between the C(1) and C(2) protons indicates an axial equatorial arrangement of these two protons and corresponds to a 2S configuration in **6**.

Three comments summarize the diastereofacial preference observed for the chloride anion addition leading to **6**. First, the result was consistent with the Arigoni's hypothesis that the attacking double bond adopts an orientation in which the π-system stabilizes the developing allylic carbonium ion.[6] Secondly, the substitution in allylic system corresponds to a syn S_N2' mechanism.[7] Finally, the carbon-carbon bond formation involves antiperiplanar addition to the double bond.[8]

Substitution of the chlorine atom of **4a**, **4b** and **6** is very difficult. Only the mixture of $(AcO)_2Hg$, BF_3 in solution in acetic acid affords respectively the acetates **7a**, **7b** and **8** in good yields (this reagent has been proposed for the substitution of vinylic chlorides).[9] As the starting material, acetate **7b** is a mixture of 2S and 2R isomers, but acetate **8** is only the 2S isomer (in ^1H NMR, the pattern of $C_{(2)}$ proton is the same one as for **6**). In this case, the substitution occurs with retention of configuration. According to the strong reactivity of the reagent and the assistance for a S_N1 mechanism, the formation of a carbocation can be involved as an intermediate which is then trapped with retention of configuration. The presence of one methyl bearing by $C_{(4)}$ on the trajectory involving in a S_N2 substitution forbids a such process.

From the acetates **7a**, **7b** and **8**, several octalones **10a**, **10b**, **11**, **14**, **15**, **16** are obtained according to the first scheme. This synthesis confirms the structure of the different compounds resulting of the cyclization of allyl-pulegols. Moreover, the ketone **11** is known as pulegone-acetone[10] and the octalone **12** is obtained by two pathways.

Ozonolysis of chlorides **4a**, **4b** or **6** leads, after treatment of the crude product by tosylic acid in benzene solution, respectively to the hexahydro-azulenones **19a**, **19b** and **20**. From **4b**, the chloro-ketol **18** can be isolated before elimination.



From the example of the allyl-pulegols, this work shows that the cyclization of 1,5-hexadien-3-ols can be an efficient process for the obtention of polycyclic interesting compounds.

Experimental Section

General Methods. ^1H NMR spectra were determined on a Varian EM 360 (60 MHz) or Varian XL 200 (200 MHz) spectrometers. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL 200 (50.309 MHz) with Me_4Si as the internal standard. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. Circular dichroism were measured on a Jouan-Roussel III instrument equipped with a Jobin-Yvon cell for the low-temperature measurements. Optical rotation were measured on a Perkin-Elmer 241 in a thermostated 10 cm cell. Melting points are uncorrected. All reactions were done under argon atmosphere.

Materials. Allyl-pulegols **2b** and **3** are obtained according to our previous works.[4]

General Procedure for the Cyclization of Allyl-Pulegols with Titanium Tetrachloride. To an ether solution (about 45 mL) of 20 mmol of allyl-pulegol stirring at -50 °C was added slowly a solution of 1.89 g (10 mmol) of $TiCl_4$ in CH_2Cl_2 (10 mL). The reaction mixture was stirred and allowed to warm to room temperature in 12 h. The reaction mixture was poured into ice. The mixture was extracted with two 50 mL portions of ether, the combined ether layers were washed with two 30 mL portions of saturated aqueous $NaHCO_3$. The ethereal solution was then dried ($MgSO_4$) and the solvent was removed with a rotatory evaporator and the crude oil was purified.

2-Chloro-4,4-Dimethyl-1,2,3,4,5,6,7,8-Octahydronaphtalene (4a). 3.60 g (20 mmol) of alcohol **2a** were used. The crude product was distilled to afford 3.37 g (85 %) of the choride **4a**. Bp 68 °C (0.3 torr). IR (film) 1285, 1225, 775 cm^{-1}; ^1H NMR (CCl_4) δ 4.40-3.78 (1, m), 1.05 (3, s), 1.02 (3, s); Found : C, 72.77; H, 9.36; Cl, 17.19 %. Calcd for $C_{12}H_{19}Cl$ C, 72.54; H, 9.57; Cl, 17.88 %.

2-Chloro-4,4,7-Trimethyl-1,2,3,4,5,6,7,8-Octahydronaphtalene (4b). 3.88 g (20 mmol) of alcohol **2b** were used. The crude oil was distilled to afford 3.6 g (85 %) of the product (which was a 1:1 mixture of 2R and 2S isomers as determined by capillary GC). Bp 75 °C (0.3 torr). IR(film) 1340, 1280, 1225, 905, 775 cm^{-1}; ^1H NMR (CCl_4) δ 4.63-3.97 (1, m), 1.03 (6, s), 0.97 (3, d J = 6.5 Hz); ^{13}C NMR δ 134.6 and 134.3 (s), 125.1 and 124.3 (s), 54.8 and 54.7 (d), 50.0 and 49.7 (t), 42.8 and 42.1 (t), 39.2 and 38.9 (t), 37.3 and 37.28 (s), 31.8 and 30.7 (t), 29.1 and 29.07 (q), 28.4 and 27.2 (d), 27.8 and 27.75 (q), 24.9 and 22.2 (t), 22.1 and 20.7 (q); mass spectrum, m/e 214 (6), 212 (19), 199 (33), 197 (100)($M^+ - CH_3$, 100)(HRMS calcd for $C_{12}H_{18}{}^{35}Cl$ 197.10969, found 197.1072), 177 (26), 161 (55), 133 (10), 119 (22), 105 (63), 91 (22).

Titanium Tetrachloride Mediated Cyclization of 2b in the Presence of Magnesium Bromide. 1,2-Dibromoethane (0.113 g, 0.6 mmol) was added to magnesium (0.016 g, 0.0067 g. atom) in anhydrous ether (10 mL). When the reaction proceeds too vigorously, the vessel is cooled with the aid of a water bath. After all the halide has been added, the reaction mixture was refluxed for 1 h. After cooling the reaction vessel at -50 °C, 3.88 g (20 mmol) of alcohol **2b** were added and a solution of 1.89 g (10 mmol) of $TiCl_4$ in CH_2Cl_2 (10 mL). The reaction mixture was stirred and allowed to warm to room temperature in 12 h. After usual work-up, the crude product is analyzed by GLC. **5** : IR (film) 1270, 1195, 905, 740 cm^{-1}; ^1H NMR (CCl_4) δ 4.63-3.97 (1, m), 1.07 (6, s), 0.97 (3, d J = 6.5 Hz); mass spectrum, m/e 258, 256, 243, 241 ($M^+ - CH_3$)(HRMS calcd for $C_{12}H_{18}{}^{79}Br$ 241.0592, found 241.0596).

(1R, 2S, 7R)-2-Chloro-1,4,4,7-Tetramethyl-1,2,3,4,5,6,7,8-Octahydronaphtalene (6). Use of the general procedure with 3 (4.16 g, 20 mmol). After the usual work-up, the crude product was chromatographed on silica gel (pentane) to afford 3.9 g (86 %) of **6**. IR (film) 1290, 1225, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.36 (1, dddd J = 13.3 Hz, J = 5.2 Hz, J = 3.4 Hz, J = 0.8 Hz), 1.12 (3, d J = 7.5 Hz), 1.06 (3, s), 0.98 (3, s), 0.95 (3, d J = 6.5 Hz); ^{13} NMR δ 133.75 (s), 130.85 (s), 59.7 (d), 43.9 (t), 40.5 (d), 38.2 (t), 37.6 (s), 31.9 (t), 29.4 (d), 28.5 (q), 27.8 (q), 24.8 (t), 22.1 (q), 14.1 (q); mass spectrum m/e 228 (7), 226 (29)(HRMS calcd for $C_{14}H_{23}{}^{35}Cl$ 226.1488, found 226.1483), 211 (100), 191 (54), 175 (94), 173 (28), 135 (31), 119 (71), 107 (21), 105 (33), 95 (21), 93 (22), 55 (25).

4,4-Dimethyl-1,4,5,6,7,8-Hexahydro-2(3H)-Naphtalenone (10a). To an acetic acid solution (about 100 mL) of 4.84 g of mercuric acetate (15 mmol) was added 1.98 g (10 mmol) of **4a**. After stirring at room temperature for 5 mn, boron trifluoride ethyl etherate is added (2.16 g, 15 mmol). After 3 h of stirring at room temperature, filtration and elimination of acetic acid under vacuum, diethylether is added and the solution is washed with saturated solution of $HNaCO_3$. The ethereal solution was then dried ($MgSO_4$), the solvent was removed with rotatory evaporator and the crude acetate is chromatographed on silica gel (ether-pentane 1/9)(1.85 g, 85 % yield). **7a** : IR (film) 1730, 1235, 1020 cm^{-1}. ^1H NMR (CCl_4) δ 5.00 (1, m), 1.96 (3, s), 1.07 (3, s), 1.00 (3, s).

An ethereal solution (30 mL) of acetate **7a** (1.98 g, 10 mmol) is slowly added to a suspension of lithium aluminium hydride (300 mg, 7,5 mmol) in ether (120 mL) cooled at -30 °C. The reaction mixture was stirred and allowed to warm at room temperature in 12 h. After usual work-up, the crude alcohol **9a** is purified by chromatography on silica gel (1.76 g, 98 % yield). **9a** : IR (film) 3450, 1110, 1030, 800 cm^{-1}; ^1H NMR (CCl_4) δ 3.80 (1, m), 1.00 (6, s).

To an acetone solution (about 50 mL) of alcohol **9a** (1.74 g, 10 mmol) stirred at -15 °C, was added 3.2 mL of Jones reagent prepared from 6.7 g of chromic anhydride, 5.75 ml of conc. sulfuric acid and 25 mL of water. The reaction mixture was stirred and allowed to warm at room temperature in 0.5 h. After one hour of stirring at room temperature and usual work-up, the crude product is purified by chromatography on silica gel (ether-pentane 1/7) to afford **10a** (1.51 g, 85 % yield) : IR (film) 1715, 1245, 800 cm^{-1}; ^1H NMR (CCl_4) δ 2.60 (2, s (broad)), 2.25 (2, s), 1.00 (6, s); Found : C, 81.08; H, 10.21 %. Calcd for $C_{12}H_{18}O$: C, 80.90; H, 10.11 %.

(R)-4,4,7-Trimethyl-1,4,5,6,7,8-Hexahydro-2(3H)-Naphtalenone (10b). Use of the same procedure described for the preparation of **7a** with 2.12 g (10 mmol) of **4b** affords **7b** (2.00 g, 85 % yield). IR (film) 1735, 1245, 1025, 790, 765 cm^{-1}; ^1H NMR (CCl_4) δ 5.23-4.63 (1, m), 1.97 (3, s), 1.10 (6, s), 0.90 (3, d J = 6.5 Hz); ^{13}C NMR (in part) δ 170.21 (s), 134.58 and 134.28 (s), 124.01 and 123.19 (s), 68.60 and 68.56 (d). Use of the same procedure described for the preparation of **9a** with 2.24 g of **7b** affords **9b** (1.9 g, 98 % yield). IR (film) 3400, 1045, 1025 cm^{-1}; ^1H NMR (CCl_4) δ 3.93-3.5 (1, m), 0.9 (6, s), 0.87 (3, d J = 6.5 Hz). Use of the same procedure described for the preparation of **10a** with 1.94 g (10 mmol) of **9b** affords **10b** (1.63 g, 85 % yield). IR (film) 1715, 1290, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57 (2, s $W_{\frac{1}{2}}$ = 6.0 Hz), 2.23 (2, d J = 3.0 Hz), 1.03 (3, s), 0.90 (3, s), 0.90 (d J = 6.5 Hz); ^{13}C NMR δ 210.64 (s), 135.77 (s), 124.35 (s), 54.90 (t), 45.16 (t), 39.18 (s), 38.87 (t), 31.62 (t), 28.66 (d), 27.47 (q), 27.17 (q), 24.70 (t), 21.68 (q); $|\alpha|_{578}^{22}$ = 162 ° (c = 16.08, hexane); Found : C, 81.12; H, 10.33 %. Calcd for $C_{13}H_{20}O$: C, 81.25; H, 10.42 %. By standing, or by heating in benzene solution with tosylic acid, ketone **10b** isomerizes in **11**.[10]

(1S, 7R)-1,4,4,7-Tetramethyl-1,4,5,6,7,8-Hexahydro-2(3H)-Naphtalenone (14). Use of the same procedure described for the preparation of **7a** with 2.26 g (10 mmol) of **6** affords **8** (2.00 g, 80 % yield). IR (film) 1735, 1245, 1025 cm^{-1}; ^1H NMR (CCl_4) δ 5.00 (1, ddd J = 13.0 Hz, J = 5.0 Hz, J = 3.5 Hz), 2.02 (3, s), 1.07-0.9 (12, m). Use of the same procedure described for the preparation of **9a** with 2.50 g (10 mmol) of **8** affords **13** (2.04 g, 85 % yield). IR (film) 3350, 1120, 1060, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.00 (1, ddd J = 10.5 Hz, J = 5.0 Hz, J = 3.0 Hz), 1.04-0.85 (12, m). Use of the same procedure described for the preparation of **10a** with 2.08 g (10 mmol) of **13** affords **14** with some proportion of **15** and **16** (1.75 g, overall yield 85 %). **14** : IR (film) 1710, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15 (2, s), 1.10 (3, d J = 7.5 Hz), 1.08 (3, s), 1.00 (3, s), 0.93 (3, d J = 6.5 Hz); mass spectrum, m/e 206 (12)(HRMS calcd for $C_{14}H_{22}O$ 206.1670, found 206.1662), 191 (1), 164 (15), 163 (100), 107 (39), 93 (14), 81 (10), 69 (10). By standing, or by heating in benzene solution with tosylic acid, ketone **14** isomerizes in ketones **15** and **16** and finally **16**. **15** : IR (film) 1695, 1670, 1650, 1260, 1245, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (2, s), 1.18 (3, s), 1.12-0.97 (9, m); mass spectrum, m/e 206 (2), 205 (2), 204 (12)(HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1518), 189 (15), 178 (41), 164 (10), 163 (100), 135 (23), 122 (13); $|\alpha|_{578}^{22}$ = 15 ° (c = 0.08, hexane). **16** : IR (film) 1665, 1085 cm^{-1}; ^1H NMR (CCl_4) δ 2.20 (2, s), 1.77 (3, s), 1.03-0.93 (9, s); mass spectrum, m/e 206 (35)(HRMS for $C_{14}H_{22}O$ 206.16170, found 206.1662), 191 (18), 175 (10), 163 (16), 150 (100), 135 (13),122 (18), 108 (30), 107 (32), 93 (18); $|\alpha|_{578}^{22}$ = -64 ° (c = 1.5, hexane).

(R)-1,1,4,4,7-Pentamethyl-1,4,5,6,7,8-Hexahydro-2(3H)-Naphtalenone (12). **a** - From **10b** : 150 mL of ammoniac are condensed in a 250 mL flask. One cristal of ferric nitrate and 0.38 g (0.54 g. atom) of lithium were added. After dissolution, ketone **10b** 4.0 g (21 mmol) are added. After 0.5 h of stirring, iodomethane (16 g, 110 mmol) was added and the reaction mixture stirred during four hours; the excess ammoniac was eliminated by distillation. After usual work-up, the ketone **12** was isolated by chromatography on silica gel (ether pentane 1/5)(3.46 g, 75 %). IR (film) 1715, 1665, 1300 cm^{-1}; ^1H NMR (CCl_4) δ 2.60 and 2.18 (2, AB pattern, J_{AB} = 12.0 Hz), 1.18-0.95 (15, m); ^{13}C NMR δ 215.27 (s), 134.73 (s), 132.59 (s), 51.50 (t), 48.05 (s), 39.29 (s), 33.29 (t), 31.33 (t), 29.00 (d), 27.87 (q), 27.51 (q), 25.81 (q), 25.26 (t), 22.50 (q), 21.79 (q); mass spectrum, m/e 220 (51)(HRMS calcd for $C_{15}H_{24}O$ 220.1827, found 220.1824), 205 (100), 187 (6), 177 (33), 163 (30), 149 (11), 121 (50), 69 (33); $|\alpha|_{578}^{22}$= 134 ° (c = 1.58, hexane).

b - From a mixture of **14**, **15** and **16** : To a THF solution (100 mL) of diisopropylamine (1.7 mL, 23.5 mmol) stirred at -30 °C, 10 mL of butyl-lithium 1.8 M were added and stirred during 0.5 h. After cooling at -70 °C, 3.2 g (16 mmol) of a mixture of ketones **14**, **15**, **16** was added. After stirring during 0.5 h, iodomethane (2,40 g, 17 mmol) was added. After 1 hour of stirring, the reaction mixture was allowed to warm to room temperature and was hydrolyzed. After usual work up, ketone **12** was isolated by chromotography on silica gel (2.37 g, 72 % yield).

(1R, 2S, 7R)-1,2,4,4,7-Pentamethyl-1,2,3,4,5,6,7,8-Octahydro-2-Naphtalenol (17). To an ethereal solution of methylmagnesium iodide (0.12 mmol), 2.06 g (10 mmol) of ketone **14** were added. After usual work-up, alcohol **17** was isolated by chromatography on silica gel (ether pentane 1/4)(2.04 g, 92 % yield). IR (film) 3600, 1145, 1095, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3, s), 1.13-0.93 (12, m); ^{13}C NMR δ 131.91 (s), 130.54 (s), 71.28 (s), 48.22 (t), 46.13 (d), 38.42 (t), 35.74 (s), 31.61 (t), 31.19 (d), 29.17 (q), 29.08 (q), 28.39 (q), 23.72 (t), 21.74 (q), 14.70 (q).

5,5-Dimethyl-1,2,3,6-Tetrahydro-4(5H)-Azulenone (19a). Ozone in oxygen was bubbled through a solution of **4a** (1.985 g, 10 mmol) in 60 mL of methanol which contained a few drops of an ethanolic solution

of "Sudan III"(Eastman Kodak)(1/10000)(4) at -60 °C until the solution turned yellow. While the solution was still at -60 °C, the system was flushed with nitrogen. The mixture was stirred at -15 °C overnight. The solvent was removed under vacuum and the crude product was chromatographed on silica gel with ether pentane (30/70)(1.06 g, 60 % yield). **19a** : Eb 84-88 °C (1 torr); IR (film) 1640, 1590, 1250, 775, 715 cm^{-1}; ^1H NMR (CCl_4) δ 6.07 (2, m), 2.70 (2, t J = 7.0 Hz), 1.03 (6, s); ^{13}C NMR δ 202.62 (s), 148.97 (s), 138.39 (s), 135.03 (d), 127.00 (d), 44.96 (s), 39.80 (t), 34.53 (t), 24.57 (q), 21.03 (t); mass spectrum, m/e 176 (47)(HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1208), 161 (20), 148 (26), 134 (95), 133 (100), 117 (30), 105 (44), 91 (42).

(S)-2,5,5-Trimethyl-1,2,3,6-Tetrahydro-4(5H)-Azulenone (19b). Use of the same procedure described for the preparation of **19a** with 2.12 g (10 mmol) of **4b**, affords **18** (ether pentane 2/3)(0.78 g, 32 % yield) and **19b** (ether pentane 3/7)(0.62 g, 32 % yield). **18** : IR (film) 3500, 1685, 1245, 1005, 985 cm^{-1}; IR, CCl_4 (2.10^{-3}) 3624 and 3612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (1, dq J = 11.6 Hz, J = 4.8 Hz), 3.37 (1, t J = 8.4 Hz), 1.31 (3, s), 1.17 (3, s), 1.06 (3, d J = 6.0 Hz); ^{13}C NMR δ 213.63 (s), 82.27 (s), 57.73 (d), 54.61 (d), 51.52 (t), 46.85 (t), 46.65 (s), 45.64 (t), 34.09 (t), 31.55 (d), 27.53 (q), 24.98 (q), 18.71 (q); mass spectrum, m/e 246 (6), 244 (16)(HRMS calcd for $C_{13}H_{21}O_2{}^{35}Cl$ 244.1230, found 244.1228), 228 (2), 226 (6), 208 (16), 191 (19), 163 (24), 138 (20), 125 (100); $|\alpha|_{578}^{22}$= 15.1 ° (c = 1.57, hexane); CD (hexane) λ_{max} = 295 nm, Θ = 5100, $\Delta\epsilon$= 1.55. **19b** : IR (film) 1630, 1585, 1255 cm^{-1}; ^1H NMR (CCl_4) δ 6.08 (2, m), 1.07 (6, s), 1.00 (3, d J = 6.0 Hz); ^{13}C NMR δ 202.48 (s), 148.03 (s), 137.55 (s), 135.05 (d), 127.13 (d), 47.63 (t), 44.91 (s), 42.43 (t), 37.32 (t), 29.69 (d), 24.73 (q), 24.38 (q), 21.09 (q); mass spectrum, m/e 190 (54)(HRMS calcd for $C_{13}H_{18}O$ 190.1357, found 190.1360), 175 (23), 162 (27), 148 (82), 147 (84), 133 (100), 105 (63); $|\alpha|_{578}^{22}$ = -5.6 ° (c = 1.69, hexane).

(S)-2,5,5,8-Tetramethyl-1,2,3,6-Tetrahydro-4(5H)-Azulenone (20). Use of the same procedure described for the preparation of **19a** with 2.26 g (10 mmol) of **6** affords **20** (ether pentane 1/6)(1.22 g, 60 % yield). **20** : IR (film) 1640, 1225, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (1, t J = 7.0 Hz), 2.48 (3 s br.), 1.8 (2, d J = 7.0 Hz), 1.08 (6, s), 1.05 (3, d J = 6.5 Hz); mass spectrum, m/e 204 (63)(HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1500), 190 (15), 189 (100), 162 (20), 161 (37), 119 (28), 105 (28); $|\alpha|_{578}^{22}$ = -22.2 ° (c = 1.46, hexane).

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(8) The Stork-Eschenmoser hypothesis for the cyclization of a 1,5-diene includes an antiperiplanar addition to the double bonds (for a discussion, see 1e).
(9) Martin, S.F.; Chou, T.S. Tetrahedron Lett., **1978**, 1943.
(10) Duc, D.K.M.; Fetizon, M.; Kone, M. Tetrahedron, **1978**, 34, 3513.