forded 428 mg of a pale yellow oil. Chromatography on 40 g of silica gel with 5% ether in hexanes afforded 218 mg (91%) of the previously reported[20] acetate **22** as a clear oil: IR (film) 1750 (C=O); NMR ($CDCl_3$) δ 7.8–7.55 (m, 2 H, aromatic), 7.55–7.2 (m, 3 H, aromatic), 7.1 (br s, 1 H, vinyl), 4.9 (s, 2 H, CH_2), 2.13 (s, 3 H, $COCH_3$).

Acknowledgment. Support of this investigation was provided by the National Science Foundation under Grant No. CHE-8111128, by the National Cancer Institute under Grant No. 27157, and by the 3M Corp. under a 3M Corp Young Faculty Grant.

Registry No. **2a**, 822-85-5; **3a**, 23029-03-0; **4a**, 56974-20-0; **7**, 50870-61-6; **8**, 10481-34-2; **9**, 5682-80-4; (*E*)-**10**, 32147-21-0; (*Z*)-**10**, 22965-96-4; (*Z*)-**11**, 33603-90-6; **12**, 83633-76-5; **13**, 83633-77-6; **14**, 83633-78-7; **15**, 83633-79-8; **16**, 83633-80-1; **17**, 83633-81-2; **18**, 83633-82-3; **19**, 83633-83-4; **20**, 83633-84-5; (*Z*)-**21**, 83633-85-6; (*Z*)-**22**, 14310-14-6; 2-cyclohexenone, 930-68-7; 2-cyclopentenone, 930-30-3; mesityl oxide, 141-79-7; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; *trans*-cinnamaldehyde, 14371-10-9; $Lime_2Cu$, 15681-48-8; Li-*n*-Bu_2Cu, 24406-16-4; Li-*n*-BuCuCN, 41742-63-6; Li(CH_2=$CH)_2Cu$, 22903-99-7; Li(*sec*-Bu)$_3$BH, 38721-52-7; Li(CH_2=CH)CuCN, 77043-46-0.

(20) Sandler, S. R. *J. Org. Chem.* **1967**, *32*, 3876.

Improved Preparation of Methyl 3-Oxo-1-cyclohexene-1-carboxylate and Its Use in the Synthesis of Substituted 1,5-Cyclodecadienes

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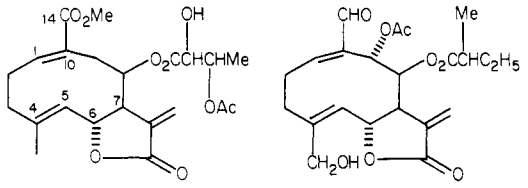
An improved preparation of methyl 3-oxo-1-cyclohexene-1-carboxylate (**6**) is reported in which cyclohexanecarboxylic acid is converted to methyl 1-bromocyclohexanecarboxylate by a variation of the Hell–Volhard–Zelinsky reaction and then the bromo ester is dehydrohalogenated with quinoline and the resultant unsaturated ester is oxidized at an allylic position with chromium trioxide in acetic acid and acetic anhydride to give **6**. The overall conversion proceeds in 49% yield, which is a substantial improvement over previous attempts reported for this sequence. Photoaddition of **6** and cyclobutene-1-carboxylic acid yields adduct **8**, which after esterification and thermolysis gives the 1,5-cyclodecadiene **12**. In addition, reduction of adduct **8** with $NaCNBH_3$ followed by spontaneous lactonization yields **10**, which upon thermolysis gives the lactone diene **11**. This approach should have applications in the synthesis of germacranolides that have an ester or related carbonyl function on C(14).

Numerous germacranolides possess oxygen functionality in the form of an ester (or lactone), an aldehyde, or a primary alcohol at C(14)[1] [e.g., melampolidin (**1**)[2] and acanthospermal B (**2**)[3]]. Many of these compounds exhibit



1 **2**

significant cytotoxic or other biological activity.[1] We wished to develop an approach to the synthesis of related 1,5-cyclodecadienes in which C(14) was present as an ester function. The approach is an extension of our previous work[4,5] employing photoaddition of a substituted cyclobutene and a 2-cyclohexenone followed by thermolysis of the photoadduct or a compound derived from it.

In our initial model studies, the ester **6** was chosen as the cyclohexenone component for the photoaddition. **6** may be prepared from cyclohexanecarboxylic acid (**3**) by bromination/esterification to give **4**[6] followed by dehydrohalogenation with collidine to yield **5**[6] and finally allylic oxidation with CrO_3 in acetic acid and water,[7] but the reported yields in the three steps are not encouraging (43%, 43%,[8] 49%, respectively).[9] We herein report a substantial improvement in the yield for the conversion of **3** to **5** and a modest improvement for the oxidation of **5** to **6**. The procedures are experimentally simple and are suitable for large-scale preparations because of the inexpensive reagents involved.

Conversion of **3** to **4** was effected in 92% yield with use of the Hell–Volhard–Zelinsky reaction followed by esterification of the resultant acid chloride in a procedure similar to that described for the preparation of a bromocyclobutanecarboxylate.[10] Dehydrohalogenation to give **5** was accomplished in 96% yield by warming **4** with 1.6 equiv of quinoline. This base has previously been used for

(1) (a) Yoshioka, H.; Mabry, T. J.; Timmermann, B. N. "Sesquiterpene Lactones"; University of Tokyo Press: Tokyo, 1973. (b) Fischer, N. H.; Frank, R. W.; Oliver, E. J. "Progress in the Chemistry of Organic Natural Products"; Springer-Verlag: New York, 1979; Vol 38, p 1.

(2) Fischer, N. H.; Wiley, R. A.; Perry, D. L.; Haegele, K. D. *J. Org. Chem.* **1976**, *41*, 3956.

(3) Herz, W.; Kalyanaraman, P. S. *J. Org. Chem.* **1975**, *40*, 3486.

(4) (a) Lange, G. L.; Huggins, M.-A.; Neidert, E. *Tetrahedron Lett.* **1976**, 4409. (b) Lange, G. L.; McCarthy, F. C. *Ibid.* **1978**, 4749. (c) Lange, G. L.; So, S.; Lautens, M.; Lohr, K. *Ibid.* **1981**, 311.

(5) For related work by others, see: (a) Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 267. (b) Williams, J. R.; Callahan, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 404. (c) Wilson, S. R.; Phillips, L. R.; Pelister, Y.; Huffman, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 7373.

(6) Bailey, W. J.; Baylouny, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 2126.

(7) W. C. Agosta and W. W. Lowrance, Jr. (*J. Org. Chem.* **1970**, *35*, 3851) employed the ethyl ester.

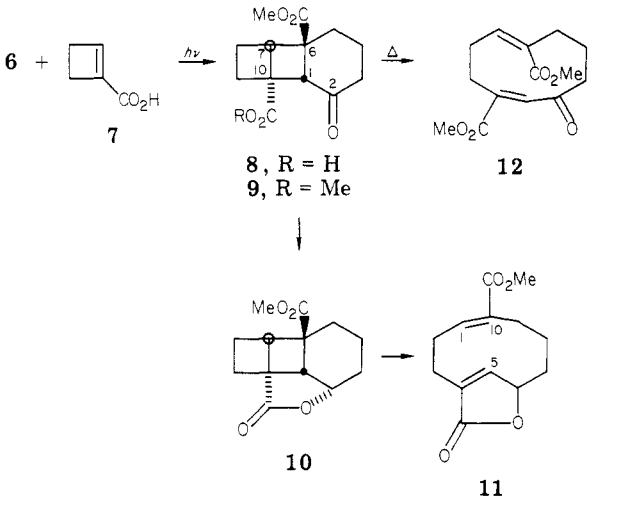
(8) R. Damico (*J. Org. Chem.* **1968**, *33*, 1550) reported a yield of 57% for the conversion of **3** to **5** following Bailey's procedure.[6]

(9) **6** or its ethyl ester may also be prepared from the cyanohydrin of cyclohexanone by dehydration followed by alcoholysis: (a) Lythgoe, B.; Trippett, S.; Watkins, J. C. *J. Chem. Soc.* **1956**, 4060. (b) Dev, S. *J. Indian Chem. Soc.* **1956**, *33*, 769.

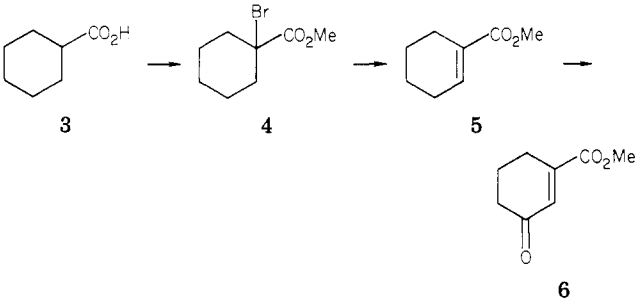
(10) Campbell, A.; Rydon, H. N. *J. Chem. Soc.* **1953**, 3002.

0022-3263/82/1947-5093$01.25/0

Scheme I



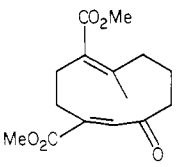
the dehydrohalogenation of acyclic α-bromo esters[11] although 5 equiv of quinoline was employed and the conditions were considerably more vigorous than those required for our system. More expensive bases such as DBN and DBU were also effective for the conversion of **4** to **5** but offered no advantage over quinoline.



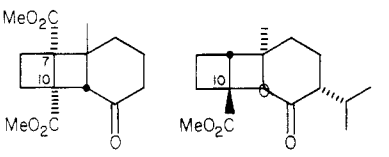
Allylic oxidation to give **6** was accomplished most effectively (56% yield) by addition of 3 mol equiv of chromium trioxide in a mixture of acetic anhydride and acetic acid *to* a solution of **5**. Allylic oxidation of methyl 2-alkenoates was previously effected by adding the ester to 5 mol equiv of chromium trioxide in the same solvent,[12] but using these conditions the yield for conversion of **5** to **6** was very low presumably because of degradation of the product. The procedure reported herein converts **3** to **5** in an overall yield of 88% and **3** to **6** in 49% yield. Thus, these versatile synthetic intermediates are now more readily available for further studies in such areas as photochemistry,[7,13] annulation,[14] Diels–Alder,[15] and conjugate addition reactions.[16]

With enone **6** in hand, we studied next its photoaddition with cyclobutene-1-carboxylic acid (**7**). Irradiation at 350 nm of a benzene solution of **6** with an excess of **7** gave adduct **8**, which was esterified with diazomethane to give diester **9** in a yield of 55% based on **6** (Scheme I). Reduction of **8** with sodium cyanoborohydride gave lactone **10** in an overall yield of 51% based on reacted **6**. The spontaneous lactone formation supported the cis-anti-cis stereochemistry assigned to the ring fusions in **8** and is consistent with structures of related cycloaddition products.[4,5] In the NMR spectra of **9** and **10** the downfield shift of the proton at C(1) (δ 3.77 singlet and 3.48 doublet, respectively) caused by the deshielding effect of the adjacent *cis*-carbomethoxyl group at C(6) further supports these stereochemical assignments.

Thermolysis of **10** at 164 °C (refluxing mesitylene) gave in good yield (85%) the crystalline cyclodecadiene **11**. The *E* configuration of the 1(10) double bond is supported by the chemical shift of the proton at C(1) (δ 6.57).[17] A similar deshielding of a β hydrogen or alkyl group by a cis ester function was noted previously.[4a] In addition, the H(1) resonance in melampolidin (**1**)[2] appears as a broadened triplet at δ 6.85. Thermolysis of diester **9** at 164 °C resulted in a 51% yield of the crystalline cyclodecadiene **12**. In this product, the H-1[17] resonance appears upfield (relative to **11**) at δ 5.68 and supports the assignment of a *Z* configuration of the 1(10) double bond. Also, the H-5 resonance appears at the same chemical shift (δ 7.07) in both **12** and the previously reported **13**[4a] and supports the proposed *E* configuration for the 4,5-double bond.



It was previously suggested[18a] that the thermolysis or cyclorevision step was facilitated by an ester group (as compared with a methyl group[18b]) at C-10 in these tricyclic adducts (e.g., **9**). A comparison indicates that adduct **14**, with ester groups at C-7 and C-10, undergoes thermolysis more readily (139 °C for 6 h)[4a] than **15** (174 °C, 10 h),[4b] which has one ester group at this ring fusion, while adduct **9** with an ester group at each ring fusion undergoes cyclorevision least readily (164 °C for 42 h). Thus, ester groups at the 7- and 10-positions accelerate the cyclorevision, possibly by stabilizing a biradical-type intermediate formed by breaking the 7,10 bond, while at the 6-position they do not accelerate the reaction.



In conclusion, thermolysis of derivatives of the photoadduct derived from enone **6** and cyclobutene **7** yield substituted cyclodecadienes in good yield. This approach should prove particularly useful in the synthesis of the melampolide [*cis*-1(10),*trans*-5-dienes] and heliangolide [*trans*-1(10),*cis*-5-dienes] subgroups of germacranolides that possess oxygen functionality at C(14).

Experimental Section

Infrared spectra were recorded on a Beckman Acculab 6 spectrophotometer, proton magnetic resonance spectra on a Varian T-60 or EM-360 spectrometer with Me_4Si (δ = 0) as internal standard, ultraviolet spectra on a Varian DMS 90 spectropho-

(11) Allen, C. F.; Kalm, M. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 608.
(12) Nakayama, M.; Shinke, S.; Matsushita, Y.; Ohira, S.; Hayashi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 184.
(13) (a) Cantrell, T. S. *J. Org. Chem.* **1975**, *40*, 1447. (b) Kropp, P. J.; Krauss, H. J. *J. Org. Chem.* **1967**, *32*, 3222.
(14) Corey, E. J.; Boger, D. L. *Tetrahedron Lett.* **1978**, 4597.
(15) Danishefsky, S.; Kitahara, T. *J. Org. Chem.* **1975**, *40*, 538.
(16) Parker, K. A.; Kallmerten, J. L. *Tetrahedron* Lett. **1977**, 4557.
(17) The germacranolide numbering system has been adopted here to simplify comparisons although the 3-carbon substituent normally present at C(7) in the natural products is absent in both 11 and 12.
(18) (a) Wender, P. A.; Hubbs, J. C. *J. Org. Chem.* **1980**, *45*, 365. (b) Williams, J. R.; Callahan, J. F. *Ibid.* **1980**, *45*, 4475.

tometer, and mass spectra on a Varian MAT CH7 or VG Micromass 7070F spectrometer. Gas chromatographic (GC) analyses were performed on an Aerograph Autoprep Model A-700 with an 8 ft by 0.25 in. column of 20% Carbowax 20M on HP 80/100 mesh Chromosorb W. Thin-layer chromatographic (TLC) analyses and separations were accomplished on silica gel GF 254 with thicknesses of 0.25 and 1.0 mm, respectively, with use of the solvent system indicated with the procedure. Medium-pressure liquid chromatography purifications used 230–400-mesh silica gel and the apparatus previously described.[19] Combustion analyses were performed by Guelph Chemical Laboratories of Guelph, Ontario.

Cyclohexanecarboxylic acid (97%) was obtained from Aldrich Chemical Co. and was used without further purification. Cyclobutene-1-carboxylic acid (7) was prepared from methyl 1-bromocyclobutanecarboxylate as previously described[10] and after crystallization from 30–60 °C petroleum ether was used immediately to minimize polymerization.

Methyl 1-Bromocyclohexanecarboxylate (4). To 52.3 g (0.408 mol) of cyclohexanecarboxylic acid in a three-necked, 500-mL, round-bottomed flask with a condenser ($CaCl_2$ drying tube), a thermometer, and a dropping funnel was added dropwise over 50 min 36.5 mL (0.500 mol) of freshly distilled thionyl chloride. The mixture was heated at 85–90 °C for an additional 2 h and then cooled to 80 °C and 0.65 g of red phosphorus was added with stirring. The temperature was increased to 90 °C and 25.6 mL (0.500 mol) of bromine was added dropwise over 100 min as the temperature was maintained below 105 °C. The mixture was heated at 100 °C for an additional 80 min and then cooled to 5 °C and 85 mL (2.1 mol) of dry methanol was added dropwise while the temperature was kept below 25 °C. The mixture was heated to reflux for 15 min and then cooled and poured into 170 mL of ice-cold water. The resultant two-phase system was extracted with ether (four times) and the organic phase was washed with 1 M $Na_2S_2O_3$ solution (once), with saturated $NaHCO_3$ solution (three times), and with saturated NaCl solution (once). The ether solution was dried ($MgSO_4$), the solvent removed under reduced pressure, and the residue distilled to yield 82.5 g (91.5%) of bromo ester **4**: bp 63–66 °C (0.6 torr) [lit.[6] bp 34–35 °C (0.15 torr)]; NMR (CCl_4) δ 1.5 (6 H, m), 2.2 (4 H, m), 3.8 (3 H, s).

Methyl 1-Cyclohexene-1-carboxylate (5). A solution of 20.0 g (90.5 mmol) of **4** and 17.1 mL (145 mmol) of distilled quinoline was heated at 120 °C with stirring under nitrogen for 60 min. After 15 min of heating a slight exothermic reaction was noted and the mixture separated into two layers. The mixture was cooled, treated with 100 mL of 20% aqueous HCl, and extracted with 30–60 °C petroleum ether (four times). The organic extract was then washed with 10% aqueous HCl, with saturated $NaHCO_3$ solution, with saturated NaCl solution, and dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave 12.2 g (96%) of the unsaturated ester **5**: bp 76–78 °C (9 torr) [lit.[8] 47–50 °C (2 torr)]; the NMR spectrum was the same as that previously reported.[8]

Methyl 3-Oxo-1-cyclohexene-1-carboxylate (6). An oxidizing solution of 10.0 g (100 mmol) of CrO_3 in 25 mL of acetic anhydride and 50 mL of glacial acetic acid (N.B., add CrO_3 to solvent mixture with cooling) was added dropwise over 35 min to a stirred solution of 4.60 g (32.9 mmol) of **5** in 50 mL of benzene at 18–20 °C. Stirring was continued at this temperature for an additional 10 min, then 50 mL of benzene was added, and the reaction mixture was cooled in an ice bath and cautiously neutralized with 100 mL of concentrated KOH solution. The two-phase mixture was poured in 200 mL of water and extracted with ether (four times). The ether extract was washed with saturated $NaHCO_3$ solution (three times) and with saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent and distillation of the residue yielded 2.84 g (56%) of ketone **6**: bp 95–100 °C (1.6 torr) [lit.[20] bp 126–128 °C (18 torr)]; IR (CCl_4) 1726, 1688, 1616 cm^{-1}; NMR ($CDCl_3$) δ 1.7–2.7 (6 H, m), 3.8 (3 H, s), 6.6 (1 H, br s). Spectroscopic properties were similar to those reported previously.[20] GC analysis of the product (200 °C) indicated the presence of trace amounts of starting ester **5** and another slightly less volatile component.

Preparation of Adduct 8. A solution of 0.76 g (4.9 mmol) of **6** and 0.69 g (7.0 mmol) of cyclobutene-1-carboxylic acid (**7**)[10] in 10 mL of benzene was placed in a Pyrex tube, degassed with nitrogen before sealing with a serum cap, and irradiated for 44 h with a Rayonet RPR 208 preparative reactor equipped with 350-nm lamps. During the irradiation the tube was held in a water-cooled immersion well to maintain a temperature of about 10 °C. GC analysis of the product mixture (200 °C) indicated 95% of **6** had reacted. The irradiation mixture was filtered through a pad of Celite to remove any polymer formed and the pad was washed with 75 mL of chloroform. The combined organic phases were extracted with $NaHCO_3$ solution (five times) and this aqueous extract was washed with 30–60 °C petroleum ether. The aqueous phase was cautiously acidified (Congo Red) with 30% sulfuric acid and extracted with diethyl ether (five times). The organic phase was washed with saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent gave 1.10 g of an oil that contained adduct **8** [IR (CCl_4) 1734, 1696 cm^{-1}] as well as some unreacted **7**. This crude adduct was used directly in the preparation of pure samples of ester **9** and lactone **10**.

Preparation of Diester 9. To a solution of 1.84 g of crude adduct **8** in dry ether was added dropwise a freshly prepared ethereal solution of diazomethane until the yellow color or CH_2N_2 persisted. The solvent was removed and the residue was purified by medium-pressure liquid chromatography with 30% ethyl acetate/30–60 °C petroleum ether (R_f 0.38) to yield 1.19 g (55% based on **6**) of crystalline diester **9**: mp 107–108 °C (from ether/petroleum ether); IR (CCl_4) 1734 (br), 1707 cm^{-1} (sh); NMR ($CDCl_3$) δ 1.50–3.05 (11 H, m), 3.62 (3 H, s), 3.75 (3 H, s), 3.77 (1 H, s); mass spectrum, m/e (relative intensity) 266 (M^+, 1), 234 (48), 206 (39), 175 (100), 147 (100).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.17; H, 6.86.

Preparation of Lactone 10. A solution of 313 mg (~1.33 mmol) of crude adduct **8** and a few crystals of methyl orange in 20 mL of dry methanol was cooled in an ice bath and to this yellow solution was added 80 mg (1.27 mmol) of $NaCNBH_3$.[21] An acidic methanol solution (stock solution: 0.2 mL of concentrated HCl in 9.8 mL of dry methanol) was added dropwise with stirring to this cooled reducing solution over a period of 3 h to maintain the acidic deep orange color (pH of 3). By this time the reduction was almost complete as judged by the limited amount of acid required to maintain the desired pH so the reaction was stirred for an additional 30 min and then the solvent was removed at reduced pressure. To this residue was added 20 mL of water and the aqueous phase was extracted with ether (five times). The ether extract was washed with saturated $NaHCO_3$ solution (three times) and with saturated NaCl solution (once) and dried ($MgSO_4$). After removal of the solvent the crude product was purified by preparative TLC with use of the solvent system 25% ethyl acetate/30–60 °C petroleum ether (R_f 0.30) to yield 135 mg (51% overall yield based on reacted **6**) of crystalline lactone **10**: mp 119–120 °C (from ether/petroleum ether); IR (CCl_4) 1769, 1734 cm^{-1}; NMR ($CDCl_3$) δ 1.30–3.10 (11 H, m), 3.48 (1 H, d, J = 10 Hz), 3.67 (3 H, s), 4.75 (1 H, br d, J = 10 Hz); mass spectrum, m/e (relative intensity) 236 (M^+, 3), 177 (43), 176 (41), 149 (35), 133 (84), 131 (97), 91 (100).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.95; H, 6.94.

Preparation of Lactone Diene 11. A mixture of 135 mg (0.572 mmol) of lactone **10** and 2 mL of freshly distilled mesitylene was refluxed for 6 h under nitrogen. The solvent was removed at 20 torr with a Kugelrohr apparatus and the residue was purified by preparative TLC with use of 40% ethyl acetate/30–60 °C petroleum ether (R_f 0.30) to give 115 mg (85%) of the lactone diene **11**, which solidified upon refrigeration: mp 66–68 °C; IR (CCl_4) 1765, 1716, 1637 cm^{-1}; NMR ($CDCl_3$) δ 1.50–2.60 (10 H, m), 3.67 (3 H, m), 5.15 (1 H, d, J = 5 Hz), 6.57 (1 H, t, J = 8 Hz), 7.07 (1 H, br s); UV (ethanol) λ_{max} 214 nm (ϵ 14 000); mass spectrum, m/e (relative intensity) 236 (M^+, 4), 177 (80), 176 (43), 133 (53), 131 (100), 91 (87).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.07; H, 6.86.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(20) Torii, S.; Kunitomi, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2349.
(21) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897.

Preparation of Diester Dienone 12. A mixture of 235 mg (0.883 mmol) of diester **9** and 2.5 mL of mesitylene was refluxed for 42 h under N_2. The solvent was removed at 20 torr with a Kugelrohr apparatus and the residue was purified by preparative TLC with the solvent system 60% ether/30–60 °C petroleum ether (R_f 0.40) to yield 119 mg (51%) of crystalline diene **12**: mp 67–69 °C; IR (CCl_4) 1721, 1702 (sh), 1685, 1634 cm^{-1}; NMR ($CDCl_3$) 1.60–3.00 (10 H, m), 3.66 (3 H, s), 3.75 (3 H, s), 5.68 (1 H, t, J = 9 Hz), 7.07 (1 H, s); UV (ethanol) λ_{max} 219 nm (ϵ 11 400); mass spectrum, m/e (relative intensity) 266 (M^+, 1), 234 (75), 207 (32), 175 (100), 147 (96), 91 (38).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.04; H, 6.95.

Acknowledgment. We acknowledge the financial assistance of the Natural Sciences and Engineering Research Council of Canada.

Registry No. **3**, 98-89-5; **4**, 3196-23-4; **5**, 18448-47-0; **6**, 54396-74-6; **7**, 23519-90-6; **8**, 83605-36-1; **9**, 83605-37-2; **10**, 83605-38-3; **11**, 83605-39-4; **12**, 83605-40-7; diazomethane, 334-88-3.

Novel Synthesis of 5,5-Dimethyl-1-octalin Derivatives

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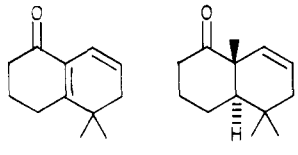
Received May 3, 1982

Pyrolysis of 3-isopropenyl-2-allylcyclohex-2-en-1-one (**4**) at ca. 275 °C yielded 3,4,5,6-tetrahydro-5,5-dimethyl-1(2*H*)-naphthalenone (**1**) as the chief product. Higher pyrolysis temperatures also yielded methyl substituted α-tetralones derived from **1**. Reductive methylation of **1** gave the trans-angularly methylated derivative **9** as the only product. The dienolate intermediate in this transformation was also trapped as a trimethylsilyl ether, **8**. Mechanisms for the pyrolytic rearrangement and the reductive alkylation are discussed.

Many terpenoid natural products incorporate fused six-membered rings bearing a *gem*-dimethyl grouping adjacent to the ring fusion. These include sesquiterpenes of the bicyclofarnesol class (e.g., drimenol), many diterpenes (labdanes, abietanes, and beyeranes among others), and virtually all triterpenes having two or more carbocyclic rings. Synthesis of this structural feature has generally been accomplished either by methylation of appropriate cyclic enones, derived in some cases from aromatic precursors[1] and in others by Robinson annulation,[2] or by acid-induced cyclization of a polyolefinic epoxide derivative.[3]

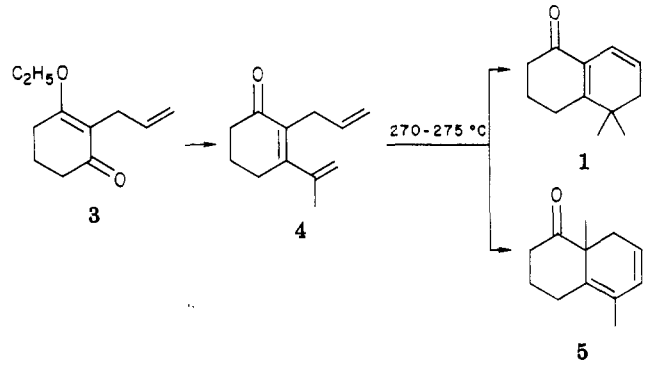
We have devised a synthesis of bicyclic ketone **1** by a novel rearrangement involving a [1, 5] sigmatropic shift of hydrogen followed by an electrocyclic ring closure. Subsequent conversion of **1** to the useful *trans*-3,4,4a,5,6,8a-hexahydro-5,5,8a-trimethyl-1(2*H*)-naphthalenone (**2**) was then achieved by a reductive alkylation sequence.



1 **2**

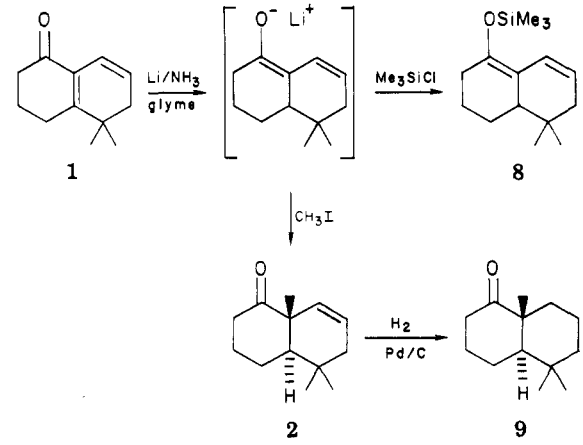
We begin with an enol ether derivative, **3**, of 2-allylcyclohexan-1,3-dione.[4] Reaction of **3** with isopropenyllithium, followed by acid hydrolysis, gave the rearrangement precursor **4** (Scheme I). Controlled pyrolysis of **4** at 270–275 °C generated **1** in 65–70% isolated yield, together with a small amount (ca. 8%) of an isomer, tentatively identified as **5**, and <2% of an unidentified contaminant which accompanies **1**. No unreacted **4** remained in the pyrolysate.

Scheme I



3 **4** **1** **5**

Scheme II



1 **8** **2** **9**

A similar pyrolysis of **4** at 290–300 °C gave a lower yield of **1** together with rearranged and demethylated products believed to be aryl ketones **6** and **7**. That the latter are

(1) Ireland, R. E.; Dawson, M. I.; Welch, S. C.; Hagenbach, A.; Bordner, J.; Trus, B. *J. Am. Chem. Soc.* **1973**, *95*, 7829 and other papers.
(2) Stork, G.; Uyeo, S.; Wakamatsu, T.; Grieco, P.; Labovitz, J. *J. Am. Chem. Soc.* **1971**, *93*, 4945 and other papers.
(3) (a) van Tamelen, E. E.; Seiler, M. P.; Wierenga, W. *J. Am. Chem. Soc.* **1972**, *94*, 8229. (b) van Tamelen, E. E.; Anderson, R. J. *Ibid.* **1972**, *94*, 8225 and other papers.
(4) Verhe, R.; Schamp, N.; DeBuyck, L.; DeKimpe, N.; sadones, M. *Bull. Soc. Chim. Belg.* **1975**, *84*, 747.

0022-3263/82/1947-5096$01.25/0