Brominations in the presence of amines were done at an amine to bromine mole ratio of 5:1. In a typical run a solution of 0.098 g of bromine, 0.24 g of pyridine, and 3.8 mL of dichloromethane was stirred at ice temperature for a few minutes and then 0.1 g of diene was added.[11] The amine was removed by extraction with cold hydrochloric acid.

Stability of Products. Several observations support our conclusion that the products obtained in the brominations and chlorinations are kinetically controlled and not equilibrated. (1) Reactions mixtures were analyzed directly by VPC with no intermediate workup. Product mixtures which varied widely in composition (and hence cannot be equilibrated mixtures) were not found to change in composition in dilute solution when stored in the refrigerator for the brief times required to complete analysis—a few days at most. Complete equilibration at room temperature required several months (entry 9, Table I). (2) Stability of the dibromides to conditions of the bromination reaction itself was demonstrated by the following experiment. Diene **6a** was brominated according to entry 17 (Table I) to give a mixture of **10a**, **12a** (with a trace of **12b**), and **14**. Solvent and excess **6a** were removed and then **6b** and dichloromethane were added along with *p*-dibromobenzene as internal standard. This mixture was analyzed by VPC after which bromine was added (conditions of entry 7). The mixture was analyzed again by VPC and the ratio of **10a** and **12a** to the internal standard was found to be the same before and after the bromination (bromination of **6b** in dichloromethane produces only traces of **10a** and **12a**), showing their stability to the reaction conditions. (3) The lack of sensitivity to hydrogen chloride produced in significant amounts by concomitant substitution in the chlorination reaction was demonstrated by an experiment done to test the effect of amines on chlorination. Chlorination of **6a** and **6b** in dichloromethane in the presence of a 10 mol excess (over chlorine) of pyridine gave dichloride product mixtures which did not differ significantly from those obtained in dichloromethane.

Analysis and Identification. Analyses of mixtures of dibromides and dichlorides were accomplished by VPC under the following conditions: 10 ft × 6 mm (o.d.) glass column packed with 2.5% SE-30 on 80–100 Chromosorb W at a temperature of 60 °C for the dibromides and 40 °C for the dichlorides. Retention times of the dibromides were (min) **10a**, 9.4, **10b**, 10.5, **12a**, 13.8, **12b**, 16.0, and **14**, 26, and of the dichlorides were (min) **16**, 3.6, **11a**, 6.6, **11b**, 7.8, **13a**, 11.8, **13b**, 13.9, and **15**, 22.2.

All of the compounds formed in the chlorination and bromination reactions were isolated by preparative VPC except for the erythro dibromide, **10b**, which was formed in such small amounts that it could not be readily obtained. Its presence was inferred because of a peak in the chromatogram very close to that of **10a**. Structures of isolated compounds were assigned on the basis of their NMR spectra. Distinctions between erythro–threo and cis–trans isomers were made on the assumptions that the major 3,4-isomer produced in the less polar solvents arises from anti addition and that the major 1,2-adduct from the trans diene has the trans structure. Proton NMR spectra (60 MHz in CCl_4 obtained with a Varian T-60A or EM-360A, parts per million downfield from $(CH_3)_4Si$) follow.

Bromination Products. 10a: 1.90 (d, 3, CH_3, $J_{4,5}$ = 6.4 Hz), 2.07 (s, 3, $CH_3CBrC{=}C$), 4.42 (q, 1, CHBr, $J_{4,5}$ = 6.4 Hz), 5.28 (d of d, 1, *cis*-HC=CH(**H**), $J_{1,2}$ = 10.2, $J_{1,1'}$ = 1.2 Hz), 5.40 (d of d, 1, *trans*-HC=C**H**(H), $J_{1',2}$ = 17, $J_{1,1'}$ = 1.2 Hz), 6.18 (d of d, 1, **H**C=CH_2, $J_{1,2}$ = 10.2, $J_{1',2}$ = 17 Hz). **12a**: 1.72 (d, 3, CH_3C-H=C, $J_{1,2}$ = 6.0 Hz), 1.78 (s, 3, $CH_3C{=}C$), 3.72 and 3.73 (d, 2, CH_2Br, J = 6.2 and 10.5 Hz), 5.2 (d of d, 1 CHBr, $J_{4,5(4,5')}$ = 6.2 and 10.5 Hz), 5.58 (q, 1, CH=C, $J_{1,2}$ = 6.0 Hz). **12b**: 1.67 (d, 3, $CH_3CH{=}C$, $J_{1,2}$ = 7.0 Hz), 1.70 (s, 3, $CH_3C{=}C$), 3.72 and 3.73 (2 d, 2, CH_2Br, J = 6.2 and 9.0 Hz), 4.72 (d of d, 1, $J_{4,5}$ and $J_{4,5'}$ = 6.2 and 9.0 Hz), 5.75 (br q, 1, CH=C, $J_{1,2}$ = 7.0 Hz). **14**: 1.78 (d, 3, CH_3CHBr, $J_{4,5}$ = 6.8 Hz), 1.87 (s, 3, $CH_3C{=}C$), 3.93 (d, 2, CH_2Br, $J_{1,2}$ = 8.0 Hz), 4.67 (q, 1, CHBr, $J_{4,5}$ = 6.8 Hz), 5.87 (t, 1, C=CH, $J_{1,2}$ = 8.0 Hz).

Chlorination Products. 11a: 1.60 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.4 Hz), 1.80 (s, 3, $CH_3CCl{=}C$), 4.17 (q,1, CHCl, $J_{4,5}$ = 6.4 Hz), 5.33 (d of d, 1, *cis*-HC=CH(**H**), $J_{1,2}$ = 10.0, $J_{1,1'}$ = 1.4 Hz), 5.47 (d of d, 1, *trans*-HC=C**H**(H), $J_{1',2}$ = 16.4, $J_{1,1'}$ = 1.4 Hz), 6.13 (d of d, 1, C**H**=CH_2, $J_{1,2}$ = 10, $J_{1',2}$ = 16.4 Hz). **11b**: 1.65 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.8 Hz), 1.73 (s, 3, CH_3CCl), 4.10 (q, 1, CHCl, $J_{4,5}$ = 6.8 Hz), 5.22 (d of d, 1, CH=CH(**H**), $J_{1,2}$ = 10.5, $J_{1,1'}$ = 1.5 Hz), 5.38 (d of d, 1, CH=C**H**(H), $J_{1',2}$ = 16.5 Hz, $J_{1,1'}$ = 1.5 Hz), 6.08 (d of d, 1, C**H**=CH_2, $J_{1,2}$ = 10.5, $J_{1',2}$ = 16.5 Hz). **13a**: 1.72 (d, 3, CH_3CH, $J_{1,2}$ = 5.2 Hz), 1.77 (s, 3, $CH_3C{=}C$), 3.68 and 3.73 (2 d, 2, CH_2Cl, J = 6.4 and 9.2 Hz), 4.98 (d of d, 1, CHCl, $J_{4,5}$ = 6.4 and 9.2 Hz), 5.58 (br q, 1, CH=C, $J_{1,2}$ = 5.2 Hz). **13b**: 1.68 (s, 3, $CH_3C{=}C$), 1.73 (d, 3, CH_3, $J_{1,2}$ = 5.0 Hz), 3.65 and 3.67 (2 d, 2, J = 6.4 and 8.8 Hz), 4.40 (d of d, 1, CHCl, $J_{4,5}$ = 6.4 and 8.8 Hz), 5.63 (q, 1, CH=C, $J_{1,2}$ = 5.0 Hz). **15**: 1.58 (d, 3, CH_3CHCl, $J_{4,5}$ = 6.5 Hz), 1.82 (s, 3, $CH_3C{=}C$), 4.02 (d, 2, CH_2Cl, $J_{1,2}$ = 8.0 Hz), 4.45 (q, 1, CHCl, $J_{4,5}$ = 6.5 Hz), 5.67 (t, 1, C=CH, $J_{1,2}$ = 8.0 Hz). **16**: 1.65 (d, 3, CH_3CHCl, J = 7.3 Hz), 4.58 (q, 1, CHCl, J = 7.3 Hz), 4.93–5.47 (m, CH=C**H**$_2$ and C=C**H**$_2$), 6.22 (d of d, 1, CH=CH_2, J = 11.3 and 18.0 Hz).

Acknowledgment. This work was supported by grants from the Research Corporation, the Catalysts of Bethany Nazarene College, and the Research Associates of Point Loma College.

Registry No. 6a, 2787-43-1; **6b**, 2787-45-3; **10a**, 75081-66-2; **10b**, 75031-74-2; **11a**, 75031-73-1; **11b**, 75081-67-3; **12a**, 75031-75-3; **12b**, 75031-76-4; **13a**, 75031-77-5; **13b**, 75031-78-6; **14**, 75031-79-7; **15**, 75031-80-0; **16**, 75031-81-1.

(11) We also carried out brominations in which the bromine–amine solution was added last to the dienes dissolved in dichloromethane. Product ratios did not differ significantly.

Syntheses of Muscone and Exaltone by Three-Carbon Ring Expansion

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Received May 30, 1980

Muscone (1) and exaltone (cyclopentadecanone) (2) are naturally occurring 15-membered cyclic ketones with a musk odor. Numerous syntheses of these cyclic ketones have been reported.[1] One important approach is the three-carbon ring expansion of easily available cyclododecanone. These attempts utilize mostly bicyclo[10.3.0]-1(12)-pentadecen-13-one (3) as a precursor, and several methods for the synthesis of this ketone and its expansion reactions have been reported.[2]

Our new method utilizes bicyclo[10.3.0]-1(15)-pentadecen-14-one (4) (Scheme I). We have previously developed a new synthetic method for 1,4-diketones and their cyclization to give cyclopentenones.[3] The method is based on the allylation of ketones and subsequent oxidation of the terminal double bond with the system $PdCl_2$–CuCl–O_2 to give 1,4-diketones, which are subjected to aldol condensation. Application of this method to cyclododecanone is expected to afford the bicyclic ketone 4. Thus, allylation of the β-keto ester 5 obtained from cyclododecanone by ethoxycarbonylation using diethyl carbonate gave 6, which was oxidized with $PdCl_2$–CuCl–O_2 in aqueous DMF to give the 1,4-diketone 7 in 72% yield from 5 (Scheme II). Aldol cyclization of the 1,4-diketone 7 using KOH in EtOH gave

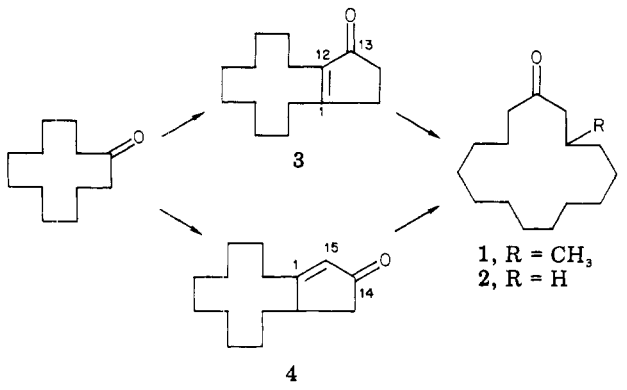
(1) For references to recent synthetic activity, see (a) C. Fehr and G. Ohloff, *Helv. Chim. Acta*, **62**, 2655 (1979); (b) G. Büchi and H. Wüest, *ibid.*, **62**, 2661 (1979); (c) K. H. Schulte-Elte, A. Hauser, and G. Ohloff, *ibid.*, **62**, 2673 (1979); (d) J. Tsuji, T. Yamada, M. Kaito, and T. Mandai, *Tetrahedron Lett.*, 2257 (1979); (e) W. E. Fristad, D. S. Dime, T. R. Bailey, and L. A. Paquette, *ibid.*, 1999 (1979); (f) S. R. Wilson and R. N. Misra, *J. Org. Chem.*, **43**, 4903 (1978).

(2) (a) G. Ohloff, J. Becker, and K. H. Schulte-Elte, *Helv. Chim. Acta*, **50**, 705 (1967); (b) A. Eschenmoser, D. Felix, and G. Ohloff, *ibid.*, **50**, 708 (1967); (c) R. W. Gray and A. S. Dreiding, *ibid.*, **60**, 1969 (1977); (d) M. Baumann, W. Hoffmann, and N. Müller, *Tetrahedron Lett.*, 3585 (1976).

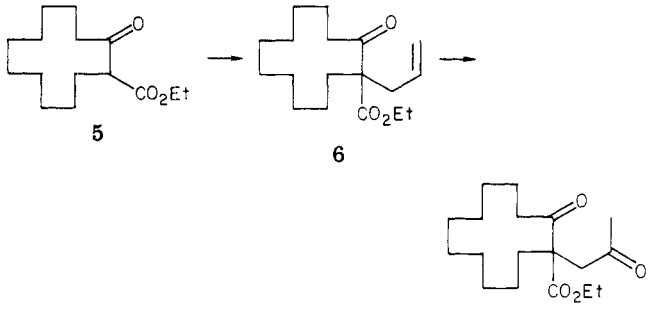
(3) J. Tsuji, I. Shimizu, and K. Yamamoto, *Tetrahedron Lett.*, 2975 (1976).

0022-3263/80/1945-5209$01.00/0

Scheme I



Scheme II



the bicyclic compound 4 in 74% yield. During this cyclization concomitant deethoxycarbonylation occurred.[4]

In order to carry out the ring expansion, the double bond of 4 must be brought from the 1(15) to the 1(12) position. This isomerization was achieved easily by acetal formation with ethylene glycol in 98% yield. The double bond of 8 was cleaved with ozone and the ozonide was reduced with $LiAlH_4$ to give the diol 9 as crystals in 86% yield after deacetalization (Scheme III). Treatment of 9 with a catalytic amount of *p*-TsOH in boiling toluene for 10 min produced the dienones 10 in 85% yield as a mixture of (*E*,*E*)-2,14-cyclopentadecadienone (**10a**) and (*E*,*E*)-2,13-cyclopentadecadienone (**10b**).[5] Hydrogenation of 10 afforded exaltone (2). The dienones 10 were treated with Me_2CuLi in ether at −25 °C to give (*E*)-3-methyl-14-cyclopentadecenone (**11a**) and (*E*)-3-methyl-13-cyclopentadecenone (**11b**) in 96% yield. Hydrogenation of the enones 11 produced (±)-muscone (1). The structure of muscone (1) and exaltone (2) was identified by comparing IR and ^1H NMR spectra with those of authentic samples and by comparison of the melting points of semicarbazones.

Experimental Section

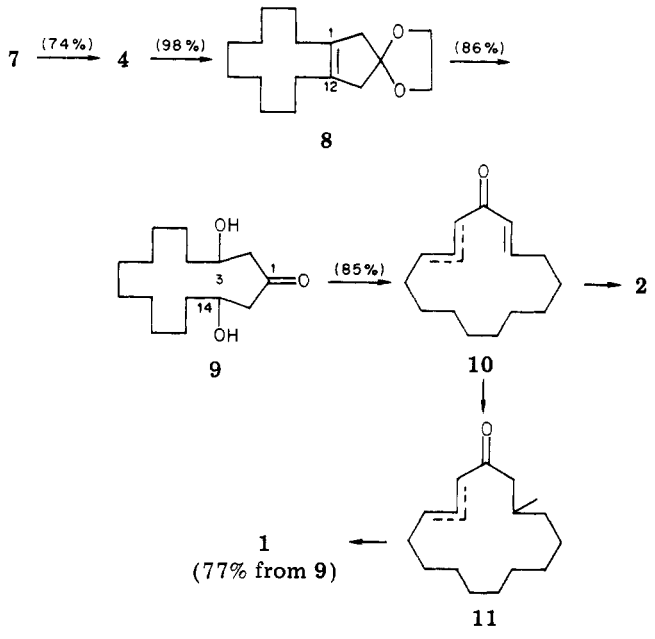
Melting points were measured on a Shibata (No 297) melting-point apparatus and are uncorrected. The IR spectra were taken on a JASCO IRA-2 spectrophotometer. The NMR spectra were taken on a Hitachi R-24A spectrometer at 60 MHz with tetramethylsilane as an internal standard.

2-(Ethoxycarbonyl)cyclododecanone (5). In a 1000-mL three-necked flask, equipped with a reflux condenser and dropping funnel, was placed a suspension of NaH (50% in mineral oil, 24 g, 0.5 mol) in dry benzene (260 mL). Diethyl carbonate (47.5 g, 0.4 mol) was added dropwise with stirring. A solution of cyclododecanone (38.5 g, 0.211 mol) in dry benzene (100 mL) was added dropwise with stirring under reflux over a period of 5 h. After the addition was completed, the reaction mixture was refluxed for an additional 1 h. Then the mixture was cooled to 0 °C. Acetic acid (40 mL) and water were added carefully. The benzene layer was separated, and the aqueous layer was extracted with benzene. The combined benzene solution was washed with aqueous $NaHCO_3$ solution and brine and dried over $MgSO_4$. After removal of the solvent, the residual oil was distilled to give 2-(ethoxycarbonyl)cyclododecanone (5, 47.6 g, 89%): bp 144–145 °C (3 torr); NMR (CCl_4) δ 4.05 (q, *J* = 7 Hz, 2 H), 3.80 (dd, *J* = 10, 4 Hz, 1 H), 2.00–2.70 (4 H), 1.20 (t, *J* = 7 Hz, 3 H), 1.10–2.00 (16 H); IR (neat) 1740, 1710 cm^{-1}.

2-Allyl-2-(ethoxycarbonyl)cyclododecanone (6). In a 300-mL three-necked flask, equipped with a reflux condenser and a dropping funnel, was placed a suspension of NaH (50% in mineral oil, 3.36 g, 70 mmol) in dry benzene (60 mL). A benzene solution of 2-(ethoxycarbonyl)cyclododecanone (5, 17.0 g, 66.9 mmol) was added dropwise at 0 °C with stirring. Then allyl bromide (9.31 g, 77 mmol) in dry benzene (20 mL) was added at reflux temperature over a period of 30 min. The resulting mixture was refluxed for an additional 5 h. After the reaction mixture was cooled to 0 °C, 3 N HCl was added. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo to give crude 2-allyl-2-(ethoxycarbonyl)cyclododecanone (6, 20.5 g), which was used in the next step without purification. The melting point and NMR data of 6 were obtained after recrystallization from EtOH: mp 56–57 °C; NMR (CCl_4) δ 4.80–5.95 (3 H), 4.15 (q, *J* = 7 Hz, 2 H), 2.40–3.10 (2 H), 1.20 (t, *J* = 7 Hz, 3 H), 0.70–2.40 (20 H).

2-(2-Oxopropyl)-2-(ethoxycarbonyl)cyclododecanone (7). In a 300-mL three-necked flask, a mixture of $PdCl_2$ (1.24 g, 7.0 mmol) and CuCl (6.93 g, 70 mmol) in aqueous DMF (60 mL of DMF and 6 mL of water) was stirred under an oxygen atmosphere for 30 min at room temperature, and 2-allyl-2-(ethoxycarbonyl)cyclododecanone (6) (20.5 g) was added. The mixture was stirred vigorously under an oxygen atmosphere for 24 h at room temperature. After the addition of 1 N HCl, the resulting mixture was extracted with ether. The extract was washed with $NaHCO_3$ solution and brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from *n*-hexane to give 2-(2-oxopropyl)-2-(ethoxycarbonyl)cyclododecanone (7, 15.6 g, 72% from 5): mp 80–81 °C; IR (KBr) 1710, 1750 cm^{-1}; NMR (CCl_4) δ 4.10 (q, *J* = 7 Hz, 2 H), 2.75–3.40 (m,

Scheme III



(4) A similar deethoxycarbonylation during aldol cyclization of a 1,4-diketone has been reported by G. Stork and F. H. Clarke, Jr., *J. Am. Chem. Soc.*, **83**, 3114 (1961).

(5) We observed that the α,β:α′,β′-unsaturated isomer **10a** was obtained at first and then isomerized to the α,β:β′,γ′-unsaturated isomer **10b** by TLC analysis. Synthesis of **10a** by condensation of 1,3-bis(dimethylphosphono)-2-propanone with 1,12-dodecadial and its isomerization to **10b** with *p*-TsOH in toluene have been reported by G. Büchi and H. Wüest (ref 1b).

2 H), 2.05 (s, 3 H), 1.50–2.35 (m, 2 H), 1.10 (t, J = 7 Hz, 3 H), 0.70–1.50 (18 H).

Bicyclo[10.3.0]-1(15)-pentadecen-14-one (4). In a 300-mL three-necked flask, equipped with a reflux condenser and a magnetic stirring bar, was placed a mixture of the diketone **7** (10.0 g, 31.5 mmol), KOH (17.6 g, 315 mmol), and EtOH (150 mL). The mixture was refluxed for 1 h and then poured into ice-cold 3 N HCl and extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ solution and brine and dried over $MgSO_4$. After removal of the solvent, the residual solid was recrystallized from EtOH to give bicyclo[10.3.0]-1(15)-pentadecen-14-one (**4**, 5.16 g, 74%): mp 95–97 °C (lit.[6] mp 95–96 °C); IR (KBr) 1720, 1610 cm^{-1}; NMR (CCl_4) δ 5.90 (s, 1 H), 2.00–3.20 (m, 5 H), 0.7–2.00 (18 H).

14,14-(Ethylenedioxy)bicyclo[10.3.0]-1(12)-pentadecene (8). A benzene solution of the enone **4** (1.00 g, 4.55 mmol), ethylene glycol, and a catalytic amount of p-TsOH was refluxed with continuous removal of water by azeotropic distillation overnight. After the mixture was cooled to room temperature, aqueous $NaHCO_3$ solution was added. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined benzene solution was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography on SiO_2 with ether–n-hexane (1:5) to give 14,14-(ethylenedioxy)bicyclo[10.3.0]-1(12)-pentadecene (**8**, 1.18 g, 98%): IR (neat) 2940 cm^{-1}; NMR (CCl_4) δ 3.80 (s, 4 H), 2.40 (s, 4 H), 1.95–2.30 (m, 4 H), 0.80–1.80 (16 H).

3,14-Dihydroxycyclopentadecanone (9). A solution of the dioxolane **8** (1.18 g, 4.47 mmol) in CH_2Cl_2 (60 mL), placed in a 100-mL three-necked flask, was treated with ozone at −60 °C. After nitrogen purge, a suspension of $LiAlH_4$ (306 mg, 8.1 mmol) in dry THF (60 mL) was added to the ozonide carefully at −20 to ~−40 °C, and the resulting mixture was allowed to warm to 0 °C with stirring. To the mixture were added EtOAc and water carefully at 0 °C with stirring, and the resulting mixture was filtered through Celite. The filtrate was poured into $NaHCO_3$ solution and extracted with CH_2Cl_2. The extract was washed with brine, dried over $MgSO_4$, and concentrated to give crude 1,1-(ethylenedioxy)-3,14-dihydroxycyclopentadecane (1.36 g) as a solid which was used in the next step without purification.

A solution of this crude material (1.36 g) and a catalytic amount of p-TsOH in aqueous THF (30 mL of THF and 30 mL of water) was refluxed for 3 h and then cooled to room temperature. After most of the THF was evaporated in vacuo, the mixture was extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ solution and brine and dried over $MgSO_4$. After evaporation of the solvent, recrystallization from ether–n-hexane (1:4) gave 3,14-dihydroxycyclopentadecanone (**9**, 983 mg, 86% from **8**) as white needles:[7] mp 103–104 °C; IR (KBr) 3300, 2920, 1700 cm^{-1}; NMR (CCl_4) δ 3.75–4.25 (2 H), 2.60–3.10 (2 H), 2.55–2.80 (4 H), 1.10–1.80 (20 H).

Muscone (1). In a 300-mL three-necked flask, equipped with a reflux condenser and a stirring bar, was placed a solution of the keto diol **9** (983 mg, 3.84 mmol) and a catalytic amount of p-TsOH in dry toluene (150 mL). The mixture was refluxed for 10 min and cooled to 0 °C. A saturated $NaHCO_3$ solution was added, and the resulting mixture was extracted with ether. The extract was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on SiO_2 with ether–n-hexane (1:5) to give an isomeric mixture of the α,β:α',β'-dienone **10a** and the α,β:β',γ'-dienone **10b** (717 mg, 85%). The mixture of **10a** and **10b** was used in the next step without separation. Pure samples were obtained from another experiment by column chromatography on SiO_2 with ether–n-hexane (1:20). (*E,E*)-2,14-Cyclopentadecadien-1-one (**10a**): TLC R_f 0.615 (Merck Kieselgel 60F_{254}, EtOAc–n-hexane, 1:3); IR (neat) 2930, 1660, 1620 cm^{-1}; NMR (CCl_4) δ 6.60 (dt, J = 7, 7 Hz, 2 H), 6.10 (d, J = 17 Hz, 2 H), 2.00–2.50 (m, 4 H), 1.00–1.80 (16 H). (*E,E*)-2,13-Cyclopentadecadien-1-one (**10b**): TLC R_f 0.692 (Merck Kieselgel 60F_{254}, EtOAc–n-hexane, 1:3); IR (neat) 2930, 1695, 1625 cm^{-1}; NMR (CCl_4) δ 6.70 (dt, J = 15, 7 Hz, 1 H), 6.05 (d, J = 15 Hz, 1 H), 5.30–5.60 (m, 2 H), 2.90–3.10 (m, 2 H), 1.80–2.45 (4 H), 0.85–1.75 (14 H).

In a 50-mL two-necked flask, equipped with a stirring bar and rubber septum, was placed completely dried CuI (2.04 g, 10.8 mmol). Dry ether (15 mL) was added to the flask, and the mixture was cooled to −25 to ~−30 °C. Then to the suspension was added MeLi (16.6 mL of a 1.18 M ethereal solution, 19.6 mmol) with stirring. The yellow solution became colorless. After the mixture was stirred for 20 min, a solution of the dienones **10** (717 mg, prepared above) in ether (10 mL) and THF (3 mL) was added over a period of 20 min to give an orange solution. The mixture was stirred for 1 h at −25 °C, and then water and 3 N HCl were added. The resulting mixture was extracted with ether, and the extract was washed with $NaHCO_3$ solution, $Na_2S_2O_3$ solution, and brine and dried over $MgSO_4$. Removal of the solvent gave a crude material which was purified by column chromatography on SiO_2 with ether–n-hexane (1:10) to afford (*E*)-3-methyl-14-cyclopentadecanone (**11a**) and (*E*)-3-methyl-13-cyclopentadecanone (**11b**) (737 mg, 96%). The IR and NMR data of **11a** and **11b** were obtained from another experiment. **11a**: IR (neat) 2930, 1690, 1620 cm^{-1}; NMR (CCl_4) δ 6.70 (dt, J = 15, 7 Hz, 1 H), 6.05 (d, J = 15 Hz, 1 H), 1.75–2.60 (m, 4 H), 0.80–1.75 (19 H), 1.00 (t, J = 6 Hz, 3 H). **11b**: IR (neat) 2930, 1710 cm^{-1}; NMR (CCl_4) δ 5.35–5.60 (m, 2 H), 2.80–3.05 (m, 2 H), 1.75–2.60 (6 H), 0.75–1.70 (17 H), 0.90 (t, J = 7 Hz, 3 H).

The mixture of **11** (737 mg) in AcOH (7 mL) was stirred in the presence of a catalytic amount of 5% Pd on C under atmospheric pressure of H_2 at room temperature. After absorption of H_2 ceased, water was added to the mixture, and the resulting mixture was extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ solution and brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on SiO_2 with ether–n-hexane (1:10) to give muscone (**1**, 708 mg, 77% from **9**): semicarbazone, mp 129.5–132.0 °C (lit.[8] mp 131–132 °C); IR (neat) 2920, 1710 cm^{-1}; NMR (CCl_4) δ 1.85–2.45 (4 H), 1.10–1.80 (23 H), 0.90 (d, J = 6 Hz, 3 H).

Cyclopentadecanone (Exaltone, 2). The cyclopentadecadienones **10** were prepared and hydrogenated by a method similar to that in the case of muscone to give cyclopentadecanone (**2**) in a quantitative yield: semicarbazone, mp 185.5–187.5 °C (lit.[9] mp 187–188 °C); IR (KBr) 2940, 1717 cm^{-1}; NMR (CCl_4) δ 2.42 (t, J = 7 Hz, 4 H), 1.45–1.90 (4 H), 1.10–1.45 (20 H).

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Registry No. **1**, 956-82-1; **1** semicarbazone, 898-26-0; **2**, 502-72-7; **2** semicarbazone, 13756-56-4; **4**, 56975-50-9; **5**, 75232-70-1; **6**, 75232-71-2; **7**, 75232-72-3; **8**, 75232-73-4; **9**, 75232-74-5; **10a**, 73125-66-3; **10b**, 73125-53-8; **11a**, 75232-75-6; **11b**, 75232-76-7; diethyl carbonate, 105-58-8; cyclododecanone, 830-13-7; allyl bromide, 106-95-6; ethylene glycol, 107-21-1; 1,1-(ethylenedioxy)-3,14-dihydroxycyclopentadecane, 75232-77-8.

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Temperature Effects on the Bromination of 2-Bromobicyclo[2.2.1]hept-2-ene. Synthesis of 2,3-Dibromobicyclo[2.2.1]hept-2-ene

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As part of our studies on the generation and reactions of bicyclo[2.2.1]hept-2-yne (norbornyne),[2] we had need of