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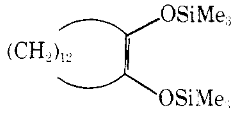
A New Synthesis of *dl*-Muscone

Yoshihiko Ito* and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Received November 22, 1976

We wish to report a convenient synthesis of *dl*-muscone (7),[1] employing as its key step the $FeCl_3$ induced ring expansion of bis(trimethylsilyloxy)bicyclo[*n*.1.0]alkanes (e.g., **3** → 4) which was found by us.[2] Our synthesis started from electrolysis of methyl hydrogen suberate producing dimethyl tetradecanedioate (1),[3] of which the silyl acyl condensation according to the Rühlmann procedure[4] afforded 1,2-bis(trimethylsilyloxy)cyclotetradecene (2). Cyclopropanation of 2 with diethylzinc and methylene diiodide[5] furnished a high yield of 1,14-bis(trimethylsilyloxy)bicyclo[12.1.0]pentadecane (3). But use of the conventional Simmons–Smith reagent, zinc–copper couple and methylene diiodide,[6] for cyclopropanation of 2 produced a complex mixture including **3**. A solution of 3 (10 mmol) in DMF (5 mL) was added to a stirring solution of anhydrous $FeCl_3$ (20 mmol) in DMF (25 mL) at room temperature, and the mixture was heated at 60 °C for 3 h. Acid workup and column chromatography on silica gel (benzene eluent) furnished cyclopentadecane-1,3-dione (4) as a keto–enol tautomer mixture in 88% yield. Conjugate addition[7] of lithium dimethylcopper to the enol acetate (5), which was readily derived by the reaction of **4** with isopropenyl acetate in the presence of *p*-toluenesulfonic acid,[8] followed by the workup with aqueous NH_4Cl and the subsequent hydrogenation with Pd/C of the resulting 3-methyl-2-cyclopentadecenone (6), yielded *dl*-muscone (7) as a light yellow oil (78%). The overall yield of *dl*-muscone from the readily available methyl hydrogen suberate is about 23%.



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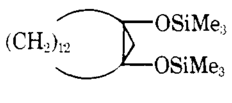

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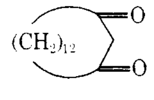

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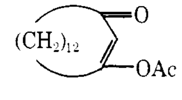

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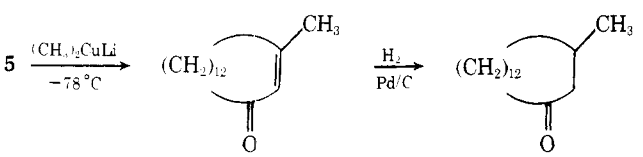

6 7

Experimental Section

Materials. Anhydrous $FeCl_3$ was prepared by treating $FeCl_3 \cdot 6H_2O$ with thionyl chloride. Diethylzinc[9] was prepared by the reaction of zinc–copper couple with ethyl iodide and ethyl bromide. Dimethyl tetradecanedioate (1) was synthesized in 65% yield by electrolysis of methyl hydrogen suberate according to the procedure[3] employed for decarboxylative dimerization of methyl hydrogen sebacate producing dimethyl octadecanedioate.

1,2-Bis(trimethylsilyloxy)cyclotetradecene (2). Under a nitrogen atmosphere, a solution of 13.7 g (48 mmol) of dimethyl tetradecanedioate (1) in 50 mL of xylene was added dropwise into a stirring mixture of a fine dispersion of molten sodium (5.75 g, 0.25 g-atom) and 28.2 g (260 mmol) of trimethylchlorosilane in 200 mL of xylene at 40–50 °C over 3 h, and then the reaction mixture was heated at reflux for 5 h. After cooling, the reaction mixture was filtered to remove sodium chloride and concentrated in vacuo. The residue was subjected to Kugelrohr distillation to afford 11.2 g (63% yield) of 1,2-bis(trimethylsilyloxy)cyclotetradecene (2): bp 100–110 °C (1 mm); IR (neat) 1672, 1250, 1210, 850 cm^{-1}; NMR (CCl_4) δ 0.14 (s, 18 H), 1.20–1.70 (m, 20 H), 1.80–2.20 (m, 4 H).

Anal. Calcd for $C_{20}H_{42}O_2Si_2$: C, 64.80; H, 11.42. Found C, 64.92; H, 11.38.

Cyclopentadecane-1,3-dione (4). Under a nitrogen atmosphere, 8.61 g (32 mmol) of methylene diiodide was added dropwise to a stirring mixture of 3.95 g (32 mmol) of diethylzinc[9] and 5.92 g (16 mmol) of 1,2-bis(trimethylsilyloxy)cyclotetradecene (2) in 50 mL of benzene at room temperature and then the mixture was heated at reflux for 3 h. The reaction mixture was worked up with aqueous NH_4Cl and extracted with benzene. The benzene extract was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Kugelrohr distillation of the residue afforded 4.98 g (81% yield) of 1,14-bis(trimethylsilyloxy)bicyclo[12.1.0]pentadecane (3): bp 110–120 °C (1 mm); IR (neat) 3070, 1250, 1220, 840 cm^{-1}; NMR (CCl_4) δ 0.12 (s, 18 H), 0.30–0.70 (m, 2 H), 0.70–2.00 (m, 24 H).

A solution of 3.84 g (10 mmol) of 3 in 5 mL of DMF was added to a stirring solution of 3.25 g (20 mmol) of anhydrous $FeCl_3$ in 25 mL of DMF at room temperature, and the mixture was heated at 60 °C for 3 h. The reaction mixture was poured into 10% aqueous HCl and extracted with chloroform. The chloroform extract was washed with 10% aqueous HCl and with water and dried over anhydrous Na_2SO_4. After the chloroform solution was evaporated, the residue was subjected to column chromatography on silica gel (benzene eluent) to furnish 2.10 g (88% yield) of cyclopentadecane-1,3-dione (4) as a keto–enol tautomer mixture. **4:** IR (neat) 1700, 1600 cm^{-1} (broad); NMR ($CDCl_3$ with Me_4Si) δ 1.44–2.00 (broad s, 20 H), 2.32–2.62 (m, 4 H), 3.68 (s) + 5.67 (s) + 15.72 (broad s) (2 H); mass spectrum M^+ *m/e* 238.

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.71; H, 11.18.

***dl*-Muscone (7).** A mixture of 2.38 g (10 mmol) of cyclopentadecane-1,3-dione (4) and 5 mL of isopropenyl acetate was heated at reflux for 3 h with 100 mg of *p*-toluenesulfonic acid.[8] The reaction mixture was poured into ice-cold water and extracted with chloroform. The chloroform extract was washed with aqueous NaCl and dried over Na_2SO_4. After the chloroform solution was evaporated, the residue was subjected to column chromatography (silica gel–chloroform) to produce 2.75 g of 3-acetoxy-2-cyclopentadecenone (5): IR (neat) 1770, 1700, 1630 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.10–1.80 (broad s, 16 H), 2.25 (s, 3 H), 2.10–2.50 (broad m, 4 H), 5.85 (s, 1 H). Lithium dimethylcopper,[7] prepared from 415 mg (2.3 mmol) of cuprous iodide and 4.6 mmol of methyllithium in 10 mL of ether at 0 °C, was added dropwise to a stirring solution of 560 mg (2.0 mmol) of **5** in 10 mL of ether, which was kept at −78 °C. The reaction mixture was stirred for an additional 30 min at −78 °C, and worked up with aqueous NH_4Cl, followed by extraction with ether. The ether extract was concentrated and subjected to the conventional hydrogenation with Pd/C. *dl*-Muscone (7, 372 mg, 78% yield) was isolated by preparative TLC on silica gel (chloroform solvent) as a light yellow oil, which was identified by comparison of its spectral data with those of an authentic sample.[10]

Registry No.—**1**, 5024-21-5; **2**, 62078-79-9; **3**, 62078-80-2; **4**, 21173-90-0; **5**, 62078-81-3; **7**, 956-82-1; trimethylchlorosilane, 75-77-4.

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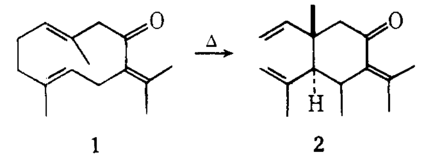
Total Synthesis of β-Elemenone

George Majetich, Paul A. Grieco,*[1] and Mugio Nishizawa

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

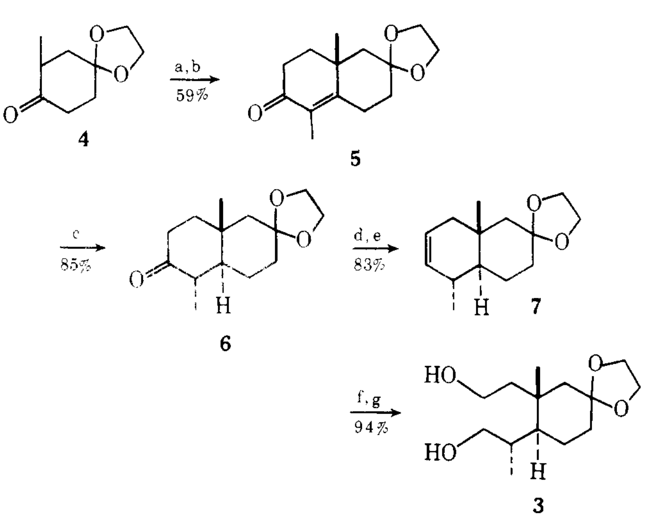
Received November 22, 1976

β-Elemenone (2) is a sesquiterpenoid isopropylidene cyclohexanone which has been isolated from Bulgarian zdravets oil[2] and *Rhododendron adamsii* Rehd.[3] The principal component of Bulgarian zdravet oil, germacrone 1,[4] undergoes smooth thermal rearrangement to β-elemenone.[2,5,6] No recorded synthesis of β-elemenone has been described. This note details the total synthesis of racemic 2 which involves a facile method for the construction of the *trans*-1,2-divinylcyclohexane unit.



The key intermediate diol 3 was prepared from 2-methyl-4-ethylenedioxycyclohexanone (4) as outlined in Chart I. Intermediate 3 possesses appropriate functionality for the introduction of the two vinyl units as well as for construction of the isopropylidene unit. The annelated product 5 has been prepared on several previous occasions from compound 4 and various ethyl vinyl ketone equivalents including ethyl vinyl ketone.[7-10] In all cases reported the overall yield of isolated ring annelated material is less than 40%.

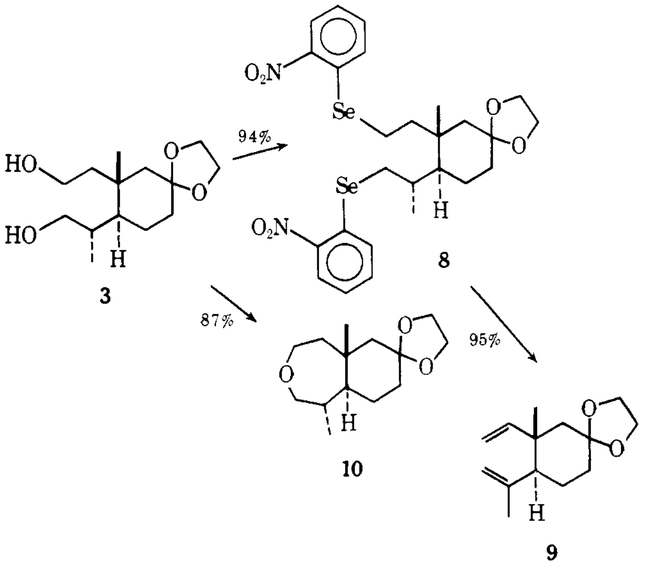
Chart I. Synthesis of Intermediate Diol 3



a, NaH, THF, $CH_3CH_2COCH_2CH_2Cl$; b, KOH, MeOH; c, Li, NH_3, *t*-BuOH, THF; d, LDA, THF, $(EtO)_2POCl$; e, Li, $EtNH_2$; f, O_3, MeOH; g, $NaBH_4$

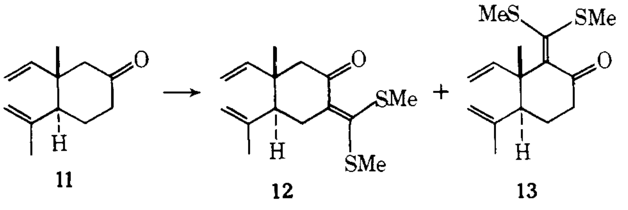
We have found that treatment of 4 with 1.3 equiv of sodium hydride in tetrahydrofuran and 1.8 equiv of 1-chloro-3-pentanone followed by treatment with methanolic potassium hydroxide gave reproducibly a 60% yield of 5 with only a trace amount of 4 remaining (see Experimental Section).

Generation of the trans ring fusion was carried out in a straightforward manner as indicated in Chart I. Introduction of the double bond in compound 6 was established by kinetic enolate formation followed by trapping of the enolate with diethyl chlorophosphate. The enol phosphate was reduced with lithium in ethylamine.[11] Ozonolysis of 7 with a sodium borohydride workup provided in very high yield intermediate diol 3, mp 61–62°.



Construction of the *trans*-1,2-divinylcyclohexane derivative 9 was carried out in a two-step process based on the method for the direct conversion of alcohols to alkyl aryl selenides.[12] Treatment of diol 3 with 2.4 equiv of *o*-nitrophenyl selenocyanate[13] in tetrahydrofuran containing 2.4 equiv of tri-*n*-butylphosphine at room temperature for 30 min gave a 94% yield of bisselenide 8 which was directly converted to diene 9 in very high yield upon treatment with 50% hydrogen peroxide in tetrahydrofuran.[14] Utilization of only 1.0 equiv of *o*-nitrophenyl selenocyanate and 1 equiv of tri-*n*-butylphosphine during an attempted conversion of 3 → 8 resulted in spontaneous formation of the seven-membered ring ether 10.

The conversion of compound 9 to β-elemenone is detailed below. Cleavage of ketal 9 under acidic conditions afforded ketone 11 which was converted to the α-dithiomethylene derivatives 12 and 13 in a ratio of 3:1 in disappointingly low yield.[15]



Reaction of 12 with 2 equiv of lithium dimethylcuprate at −78 °C produced β-elemenone in 90% yield. The NMR spec-