intermolecular shielding cannot be ruled out. This possible association between carbamyl and phosphoryl moieties of compound 8 can be disrupted only by relatively drastic reaction conditions (anhydrous $Et_3N$, 50 °C, 8 h). Compound 8 is stable to treatment with water (reflux, 1 h) but decomposes on heating in dilute aqueous base.

In summary, we present evidence for the isolation of a relatively stable glycerophosphochloridate (8). What at first glance appears to be a relatively straightforward reaction, on closer examination yields some rather interesting structural and mechanistic results. Elemental analysis, $^1H$ NMR, and $^{31}P$ NMR data are consistent with the proposed structure. The stability of the P–Cl bond appears to be intimately connected to shielding of the phosphochloridate by the methylcarbamyl moiety on the adjacent *sn*-2 glycerol carbon atom. The phosphochloridate can be converted to the corresponding phosphate by heating with anhydrous $Et_3N$.

## Experimental Section

**General Methods.** All chemicals were used as supplied without further purification unless indicated. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. FAB-MS were obtained on a VG-7070EQ spectrometer in a glycerol matrix. IR spectra were obtained on a Perkin-Elmer 1320 infrared spectrometer. $^1H$ NMR spectra were taken at ambient temperature with chemical shifts expressed as ppm downfield from $Me_4Si$ as an internal standard on either a JEOL-FX-60 or Bruker 250-MHz spectrometer. The $^{31}P$ NMR experiment was performed on a Varian XL-400 spectrometer with 85% $H_3PO_4$ as an external standard. TLC data were determined on either Bakerflex I-BF or Analtech silica gel chromatographic plates in the indicated solvent systems. Column chromatography was performed with Merck silica gel, 230–400 mesh, in the indicated solvent systems.

***rac*-1-*O*-Hexadecyl-3-*O*-tritylglycerol (5).** The procedure of Baumann and Mangold[13] was employed to provide 4 in 92% yield (mp 64–65 °C; lit. mp 65.5 °C). Compound 4 was tritylated according to Heymans et al.[14] to produce 5 in 56% yield as a white solid, mp 56–58 °C.

***rac*-1-*O*-Hexadecyl-2-*O*-(methylcarbamyl)glycerol (7).** The procedure of Gupta and Bali[1] was employed to introduce the methylcarbamate moiety. To a solution of 5 (9.0 g, 16 mmol) and 4-(dimethylamino)pyridine (2.07 g, 17 mmol) in $CH_2Cl_2$ (50 mL) was added the methyl isocyanate (4.85 g, 85 mmol). The reaction vessel was flushed with $N_2$ and sealed and the contents were stirred in the dark at room temperature. After 72 h, the volatiles were removed with a rotary evaporator, resulting in 15.2 g of crude product as an orange oil. Chromatography on 150 g of silica gel ($Et_2O$) resulted in 10.1 g of slightly impure yellow oil [$R_f$ ($Et_2O$) 0.44]. The trityl group was removed[15] and the viscous yellow oil purified by chromatography (95/5 $CHCl_3$/MeOH), resulting in 3.7 g of product 7 (62% from 5) as a white solid [$R_f$ (95/5 $CHCl_3$/MeOH) 0.59], mp 59–60 °C]: IR 1690 $cm^{-1}$, 3450, 3330; FAB-MS, $m/z$ (M + 1) 374.

***rac*-1-*O*-Hexadecyl-2-*O*-(methylcarbamyl)glycero-3-phosphorochloridocholine (8).** A solution of alcohol 7 (1.5 g, 4 mmol) and $Et_3N$ (0.5 g, 5 mmol) in 40 mL of $CH_2Cl_2$ was added to freshly distilled $POCl_3$ (0.77 g, 5 mmol) cooled to 4 °C in an ice bath under an atmosphere of nitrogen. The resulting solution was stirred for 0.5 h, at which time it was warmed to room temperature. After the addition of 2.0 mL of pyridine and solid choline tosylate[15,16] (2.43 g, 8.8 mmol), the solution was stirred at room temperature for 5 h followed by the addition of 2.0 mL of $H_2O$ and continued stirring for 2 h. The volatiles were removed with a rotary evaporator, and the resulting semisolid was taken up in $CH_2Cl_2$ (50 mL) and washed with 2 × 20 mL of $H_2O$, 5 × 25 mL of 5% HCl, and 3 × 25 mL of $H_2O$, using MeOH to break the emulsions. The nonaqueous layer was dried ($MgSO_4$) and filtered, and volatiles were removed with a rotary evaporator to give 1.6 g of crude material. Chromatography on 10 g of silica gel (50/25/8/4 $CHCl_3$/MeOH/HOAc/$H_2O$) followed by acetone precipitation and drying of the resulting solid under high vacuum/KOH resulted in 617 mg (28%) of pure product (C, H, N):[17] FAB-MS, $m/z$ (M + 1) 557, (M + 3) 559; IR 1697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 0.88 (3 H, t, $CH_3$), 1.26 (26 H, t, $-CH_2-$), 1.52 (2 H, dt, $\beta$-$CH_2$), 3.1 (3 H, d, $CH_3N$), 3.35 (9 H, s, $N(CH_3)_3$), 3.42 (4 H, m, $-CH_2-$, 1-$CH_2O$), 3.52 (m, 2 H, 3-$CH_2O$), 3.65 (1 H, m, -NH-), 3.85 (2 H, m, $-CH_2N$), 4.32 (2 H, dm, $POCH_2$), 4.98 (1 H, m, CH).

**Synthesis of 2 from the Lyso Phospholipid 3.** The lyso phospholipid 3 (100 mg, 0.2 mmol) was converted to the acid form 10 by a modified Bligh and Dyer[18] extraction procedure. After removal of solvent under a $N_2$ stream and drying under vacuum/$P_2O_5$, the lyso phospholipid was taken up in 4 mL of DMF. Methyl isocyanate (0.5 mL) was added and the reaction mixture stirred at 50 °C for 5 h. Volatiles and solvent were removed under vacuum and chromatography on silica gel (70/35/7 $CHCl_3$/MeOH/$NH_4OH$) resulted in 75.5 mg (70%) of 2 as a white powder after acetone precipitation: FAB-MS, $m/z$ (M + 1) 539; $^1H$ NMR 2.75 (3 H, d, $CH_3N$).

**$^{31}P$ NMR Experiment.** To a 10-mm NMR tube was added 12.3 μL (1.25 equiv) of $POCl_3$ and 3 mL of $CDCl_3$. A reference spectrum was obtained. A solution of 50 mg of 7 (1.0 equiv, 0.13 mmol) and 19 μL (1.25 equiv) of $Et_3N$ in 2 mL of $CDCl_3$ was added to the NMR tube and the shift in $^{31}P$ NMR signal monitored for 1.0 h. $Et_3N$ (0.1 mL) and choline tosylate (0.1 g, 2.75 equiv) were added to the reaction tube and spectra were obtained over a 5-h period. Pyridine (0.1 mL) was added to the reaction tube and spectra were obtained at 5-min intervals for 30 min. The reaction was allowed to proceed at ambient temperature overnight. Another spectrum of the reaction product was obtained and $H_2O$ (0.3 mL) was added to the reaction tube. A final spectrum was obtained after 30 min.

**Acknowledgment.** We thank Dr. David Harris (UNC Chemistry Department) for performing the $^{31}P$ NMR experiment and Dr. David Millington (Duke University Medical Center, Pediatric Metabolism and Genetics Division) for obtaining the FAB-MS and helpful discussions. We thank M. Ellis for his work on this project. Discussions with and suggestions made by Professor Fausto Ramirez were most helpful. This work was supported by NIH Grant HL-28491 and Grant HL-26818.

**Registry No.** 2, 111057-91-1; 3, 17364-21-5; 4, 6145-69-3; 5, 82002-20-8; 6, 112247-71-9; 7, 112247-72-0; 8, 112247-73-1; 10, 112247-74-2; $HOCH_2CH_2N^+Me_3 \cdot TsO^-$, 55357-38-5.

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# Intermolecular Diels–Alder Reactions of 3-Vinylcyclohex-2-en-1-ol and a Silyl Ether Derivative[1]

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*Received June 24, 1987*

The dienol system 1 and related derivatives have proven to be valuable building blocks in the total synthesis of

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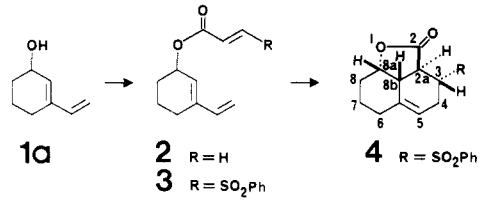
**Scheme I**

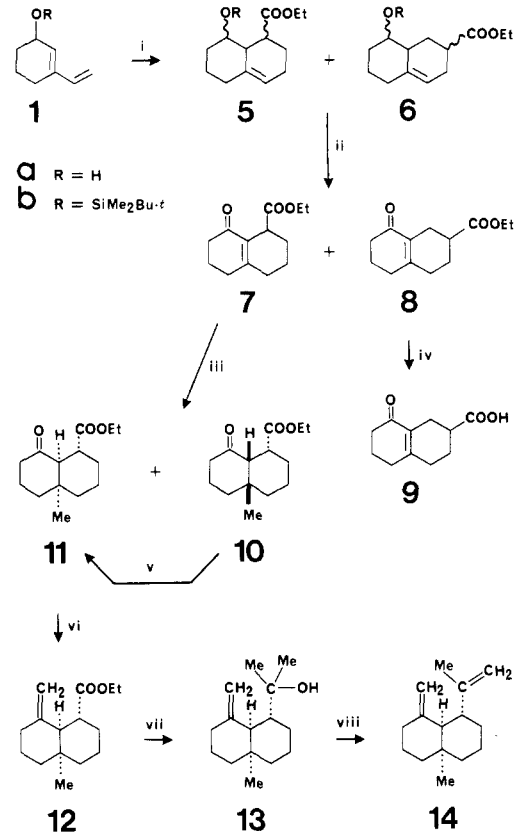



natural products via intramolecular cycloadditions.[3-5] For example, the intramolecular Diels–Alder reaction between the diene portion of a suitably substituted derivative of **1** and a dienophilic component attached to the hydroxyl group through an ester or ether linkage has been utilized in several synthetic approaches to forskolin[3] as well as a total synthesis of platyphyllide.[4] Given that the geometry of the transition state for intramolecular cycloaddition in such molecules having a short diene–dienophile bridge is controlled by nonbonded interactions, rather than electronic factors,[5] it seems reasonable that these same steric constraints are responsible for the generally low reactivity of molecules that do not have a doubly activated dienophile component.[3a,5b] These generalizations are illustrated below by our previously unreported and independent studies of the thermolysis of unactivated acrylic ester **2** and its β-sulfonyl derivative **3** (Scheme I). The sulfonyl ester **3** was smoothly cyclized to a single, tricyclic lactone **4** at 105 °C, but the acrylate **2** was highly resistant to thermolysis even at 170 °C.[6]

As an extension of our studies on synthetic applications of **1**, we wish to report facile intermolecular cycloadditions of ethyl acrylate with alcohol **1a** and its sterically hindered *tert*-butyldimethylsilyl ether derivative **1b**. The two reactions exhibit opposite (head-to-head or head-to-tail) regioselectivities as a result of predominant steric control in the cycloaddition to **1b**. In addition, we wish to demonstrate that these cycloaddition reactions provide the basis for stereospecific entries into *cis*- and *trans*-decalin systems.

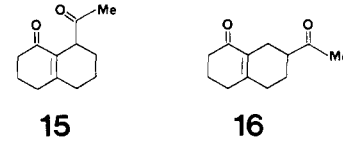
Heating of **1a** with excess ethyl acrylate produced a complex mixture of isomeric hydroxy esters **5a** and **6a**; however, Swern oxidation of this mixture, followed by acid-catalyzed isomerization of the β,γ-double bond, afforded keto ester **7** as a major product (53% based on **1a**) together with regioisomer **8** (21%). The α,β-unsaturated keto esters **7** and **8** were easily separated by using silica gel chromatography. In a similar manner cycloaddition of silyl ether **1b** with ethyl acrylate followed by desilylation of the resultant adducts **5b** and **6b** and subsequent oxidation/isomerization produced **7** as the minor product (26%) and **8** as the major keto ester (41%). Thus, either **7** or **8** can be prepared as the major product. Modest yields are obtained, but this inconvenience is offset by the simplicity of the experimental procedure.[7]

**Scheme II**[a]




[a] Key: (i) $CH_2$=CHCOOEt, *p*-$C_6H_4(OH)_2$, toluene, 105 °C; (ii) **5a** and **6a**, DMSO, $(COCl)_2$, $Et_3N$, dichloromethane, −50 °C, followed by 6 N HCl; (ii) **5b** and **6b**, $CH_3COOH$, $H_2O$, room temperature, then DMSO, $(COCl)_2$, $Et_3N$, dichloromethane, −50 °C, followed by 6 N HCl; (iii) **7**, $Me_2CuLi$, ethyl ether, 0 °C; (iv) **8**, NaOH, $H_2O$, 80 °C; (v) *p*-TsOH, benzene, 55 °C; (vi) $(Ph)_3PCH_2$, DMSO, 40 °C; (vii) MeLi, ethyl ether, 0 °C; (viii) $SOCl_2$, pyridine, 0 °C.

The isomeric octalone esters **7** and **8** are of synthetic significance in that they can be transformed into decalins with the cis and trans skeletons, respectively. The synthetic utility of **8** and its parent acid[8] **9** for the preparation of several members of the eudesmane family of sesquiterpenes containing primarily a trans-fused decalin system has been demonstrated previously.[8,9] A similar strategy

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(6) Two isomeric tricyclic lactones were obtained in low yields (ca. 20%) at higher temperatures. The structures and chemistry of these lactones are currently under investigation.

(7) Synthetic entry into the octalone skeleton using diene **1a** or **1b** was less successful with methyl vinyl ketone as the dienophile. The adducts of **1a** with methyl vinyl ketone were oxidized (Swern oxidation) and rearranged (37% $HCl/CH_2Cl_2$, 40 °C, 30 min) to produce ketone **15** [18%; $^1H$ NMR (60 MHz) δ 3.62 (1H, m, H8a), 2.9–1.4 (15 H, m including s at δ 2.30 for Me); HRMS calcd for $C_{12}H_{16}O_2$ *m/e* 192.1151, found *m/e* 192.1148], and ketone **16** [25%; $^1H$ NMR (60 MHz) δ 2.9–1.2 (m including s at δ 2.24 for Me); HRMS calcd for $C_{12}H_{16}O_2$ *m/e* 192.1151, found *m/e* 192.1149]. Lower yields of **15** and **16** were obtained with the silyl derivative **1b** as the starting material; however, no attempt was made to optimize the yields in the critical cycloaddition step.

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applied to the previously unknown octalone **7** results in cis-fused decalins, as exemplified in Scheme II by the synthesis of 8,9-*epi*-β-gorgonene (**14**).

In contrast to the octalone ester **8** (or acid **9**)[8] the ethoxycarbonyl group in **7** exerts a pronounced effect on the stereochemical outcome of conjugate addition to the 9,10-carbon–carbon double bond. Thus, treatment of **7** with lithium dimethylcuprate in diethyl ether at 0 °C followed by careful quenching of the resulting enolate with aqueous ammonium chloride at 0 °C provided a 55:45 kinetic product distribution of the epimeric *cis*-decalone esters **10** and **11** in 90% yield. Chromatographic separation of these epimers was surprisingly easy and may be ascribed to the rather different spatial relationships of the ester substituents. The structures of **10** and **11** were assigned on the basis of the $^1$H NMR coupling patterns for the appropriate methinyl protons with verification provided by proton NOE spectra. Only traces of a third addition product, ascribable to a trans-fused decalone structure, was detected.[10] Treatment of the original mixture of **10** and **11** with acid produced the thermodynamically more stable *cis*-decalone **11** as the sole isomer in the equilibration medium.[10] Wittig methylenation of **11** followed by the reaction of the resultant compound **12** with methyllithium furnished tertiary alcohol **13**. Dehydration of **13** produced 8,9-*epi*-β-gorgonene (**14**) in a 20% overall yield based on **1a**. Analyses of the NOE $^1$H NMR spectra for **14** revealed the identical stereochemistry[11] as that found for keto ester **11**.

## Experimental Section

All NMR spectra were taken in a $CDCl_3$ solution with $Me_4Si$ as an internal standard. $^1$H NMR spectra were recorded on Varian EM360 (60 MHz) and Nicolet NT-300 (300 MHz) spectrometers. $^{13}$C NMR spectra were recorded on the Nicolet spectrometer. Mass spectra were obtained with 70-eV ionizing energy.

All Diels–Alder reactions and preparations with organometallic reagents were conducted in dry solvents under an argon atmosphere. Ether and THF were distilled from sodium benzophenone ketyl.

**3-Vinylcyclohex-2-enyl Acrylate (2).** A solution of freshly distilled **1a**[4] (500 mg, 4.03 mmol, bp 80 °C (0.2 Torr)) in ether (125 mL) was treated with *n*-BuLi (1.6 M, 2.65 mL, 4.24 mmol) at −78 °C for 5 min. After 10 min, acryloyl chloride (0.35 mL, 4.24 mmol) was added within 10 min while the bath temperature was maintained at −78 °C. The reaction mixture was allowed to warm to −30 °C over 1 h and then to 0 °C over 30 min and then quenched with water and extracted with ether (3 × 50 mL). Chromatography on silica gel (EtOAc–hexanes, 5:95) afforded 0.67 g (94%) of **2**: mass spectrum, *m/e* (relative intensity) 178 (2, $M^+$), 123 (8), 106 (59), 91 (100); $^1$H NMR (60 MHz) δ 6.8–5.1 (8 H, m), 2.4–1.5 (6 H, m); HRMS calcd for $C_{11}H_{14}O_2$ *m/e* 178.0994, found *m/e* 178.0992.

**3-Vinylcyclohex-2-enyl (*E*)-β-(Phenylsulfonyl)acrylate (3).** A solution of (*E*)-β-(phenylsulfonyl)acrylic acid[12] (414 mg, 2 mmol) and oxalyl chloride (1 mL) in benzene (4 mL) was heated at 60 °C for 12 h. Evaporation of excess oxalyl chloride and benzene under reduced pressure gave a crystalline residue of the acid chloride, which was dissolved in ether and allowed to react with a lithium derivative of **1a** as described above. Chromatography on silica gel (EtOAc–hexanes, 1:9) afforded 373 mg (59%) of **3**: $^1$H NMR (60 MHz) δ 8.25–7.45 (5 H, m), 7.55 (1 H, d, *J* = 16 Hz) 7.00 (1 H, d, *J* = 16 Hz), 6.80–5.00 (5 H, m), 2.40–1.50 (6 H, m). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 63.84; H, 5.58.

**(2aα,3α,8aβ,8bβ)-2a,3,4,6,7,8,8a,8b-Octahydro-3-(phenylsulfonyl)-2*H*-naphtho[1,8-*bc*]furan-2-one (4).** A solution of **3** (100 mg, 0.31 mmol) and hydroquinone (5 mg) in toluene (20 mL) was heated at 105 °C for 20 h. Chromatography on silica gel (EtOAc–hexanes, 1:1) and then crystallization (chloroform–hexanes, 1:9) gave 63 mg (63%) of **4**: mp 221–222 °C; $^1$H NMR (300 MHz) δ 7.96–7.54 (5 H, m, Ph), 5.58 (1 H, m, H5), 4.59 (1 H, m, $J_{8-8a}$ = 5 and 12 Hz, $J_{8a-8b}$ = 8 Hz, H8a), 3.75 (1 H, m, $J_{2a-3}$ = 10.1 Hz, $J_{3-4}$ = 3.3 and 10 Hz, H3), 3.00 and 2.95 (2 H, 2 m, $J_{4-4}$ = 16.5 Hz, H4), 2.83 (1 H, m, $J_{2a-8b}$ = 13.7 Hz, H8b), 2.70 (1 H, 2 d, H2a), 2.38, 2.07, 1.89, and 1.51 (6 H, 4m); IR (KBr) 2988, 2910, 1770, 1642 cm$^{-1}$. Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.20; H, 5.67.

**3-(*tert*-Butyldimethylsiloxy)-1-vinyl-1-cyclohexene (1b).** A mixture of **1a**[4] (500 mg, 4.03 mmol) and sodium hydride (106 mg, 4.42 mmol) in THF (40 mL) was stirred at 0 °C for 30 min and then treated with a solution of *tert*-butyldimethylsilyl chloride (665 mg, 4.42 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then quenched with water and extracted with ether (3 × 50 mL). The extract was washed with a saturated solution of NaCl, dried ($Na_2SO_4$), and concentrated. Chromatography on silica gel (hexanes) was followed by Kugelrohr distillation [80 °C (5 Torr)] to afford 797 mg (83%) of **1b**: $^1$H NMR (60 MHz) δ 6.57–4.90 (5 H, m), 2.40–1.30 (6 H, m), 0.90 (9 H, s), 0.09 (6 H, s); HRMS calcd for $C_{14}H_{26}OSi$ *m/e* 238.1754, found *m/e* 238.1757.

**Ethyl 1,2,3,4,5,6,7,8-Octahydro-8-oxo-1-naphthalenecarboxylate (7). A.** A mixture of **1a** (1 g, 8.06 mmol), hydroquinone (20 mg), ethyl acrylate (5 mL, 46 mmol), and toluene (5 mL) was heated at 105 °C for 20 h and then the excess ethyl acrylate and toluene were removed [50 °C (1 torr)]. Swern oxidation[13] of the resultant hydroxy esters **5a** and **6a** was conducted in dichloromethane (50 mL) with DMSO (2.5 mL, 35.2 mmol), oxalyl chloride (1.4 mL, 16 mmol), and triethylamine (10 mL). A solution of crude oxidation products was washed with hydrochloric acid (6 N, 3 × 50 mL), water, and a solution of $NaHCO_3$ and then dried ($Na_2SO_4$). Chromatography on silica gel (EtOAc–hexanes, 1:9) afforded **8** (376 mg, 21%) and **7** (948 mg, 53%) as colorless oils in order of elution.

**B.** The reaction of **1b** with ethyl acrylate was conducted as described above to give a mixture of silyloxy esters **5b** and **6b**. Desilylation in aqueous acetic acid (75%, room temperature, 24 h) was followed by oxidation of the resultant hydroxy esters, and then workup as described above to produce **7** (26%) and **8** (41%).

**Keto ester 7**: mass spectrum, *m/e* (relative intensity) 222 (4, $M^+$), 177 (25), 176 (66), 149 (100); $^1$H NMR (60 MHz) δ 4.18 (2 H, q, *J* = 7 Hz), 3.52 (1 H, m), 2.7–1.5 (12 H, m), 1.25 (3 H, t, *J* = 7 Hz); $^{13}$C NMR δ 197.2, 174.9, 158.4, 130.1, 59.8, 38.3, 36.9, 30.8, 25.7, 21.5, 18.9, 13.6; IR (neat) 1730, 1663, 1601 cm$^{-1}$. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.06; H, 8.20.

**Ethyl 1,2,3,4,5,6,7,8-octahydro-8-oxo-2-naphthalenecarboxylate (8)**: mass spectrum, *m/e* (relative intensity) 222 (61, $M^+$), 149 (81), 120 (100); $^1$H NMR (60 MHz) δ 4.26 (2 H, q, *J* = 7 Hz), 3.0–1.5 (13 H, m), 1.28 (3 H, t, *J* = 7 Hz).

**1,2,3,4,5,6,7,8-Octahydro-8-oxo-2-naphthalenecarboxylic Acid (9).** A mixture of **8** (222 mg, 1 mmol), THF (10 mL), and aqueous NaOH (2 N, 10 mL) was stirred at 80 °C for 1 h, then cooled, acidified to pH 4 with hydrochloric acid, and extracted with ether (4 × 50 mL). Chromatography on silica gel (ether–hexanes, 1:1) and then crystallization from aqueous acetonitrile afforded **9** (126 mg, 65%) as a white solid: mp 145–147 °C (lit.[8a] mp 146–147 °C, lit.[8b,c] mp 145–146 °C);

**Ethyl (1α,4aβ,8aβ)-4a-Methyl-8-oxodecahydronaphthalene-1-carboxylate (10).** A solution of lithium dimethylcuprate in ether (10 mL), prepared[14] from $Me_2S$·CuBr (0.78 g, 3.79 mmol) and methyllithium in ether (1.5 M, 5 mL, 7.5 mmol),

(10) The essential absence of trans-fused isomers can be understood in terms of unfavorable steric interactions that would involve the ethoxycarbonyl substituent; for analysis of a similar system see: House, H. O.; Thompson, H. W. *J. Org. Chem.* **1963**, *28*, 360.

(11) For previous synthesis of **14**, see: Boeckman, R. K., Jr.; Silver, S. M. *J. Org. Chem.* **1975**, *40*, 1755. The observed differences in the $^1$H NMR spectra of **14** obtained in this work ($CDCl_3$, 300 MHz) and reported by Boekman and Silver ($CCl_4$, 60 MHz) may be accounted for by the different conditions in recording the data.

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(13) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

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was treated with 7 (0.23 g, 1.04 mmol), and the resultant mixture was stirred at 0 °C, for 3 h and then at +5 °C for 2 h. The mixture was poured into a well-stirred, cold solution of ammonium chloride and ammonia (5% each, 100 mL) and extracted with ether. Chromatography on silica gel (EtOAc–hexanes, 3:97) afforded **11** (100 mg, 41%), which was eluted first, and **10** (123 mg, 50%) as colorless oils.

**Keto ester 10**: $^1$H NMR (300 MHz) $\delta$ 4.12 (2 H, q, $J$ = 7 Hz, Et), 2.98 (1 H, m, H5$\alpha$), 2.44 (1 H, 4 d, $J_{1-2}$ = 14 and 2 Hz, $J_{1-8a}$ = 6 Hz, H1), 2.33 (1 H, d, $J_{1-8a}$ = 6 Hz, H8a), 2.3–1.4 (11 H, m), 1.27 (3 H, $J$ = 7 Hz, Et), 1.06 (3 H, s, Me); an $^1$H NOE enhancement at $\delta$ 2.33 (H8a) was observed upon irradiation at $\delta$ 1.06 (Me); $^{13}$C NMR $\delta$ 209.2, 173.8, 60.0, 59.0, 42.7, 41.2, 40.2, 38.0, 37.2, 28.8, 20.8, 20.7, 18.5, 14.1; IR (neat) 1730 cm$^{-1}$; HRMS calcd for $C_{14}H_{22}O_3$ $m/e$ 238.1570, found $m/e$ 238.1573.

**Ethyl (1$\alpha$,4a$\alpha$,8a$\alpha$)-4a-Methyl-8-oxodecahydronaphthalene-1-carboxylate (11).** In addition to the preparation described above, compound **11** was obtained in the two following isomerization reactions.

**A.** A solution of **10** (100 mg) and $p$-toluenesulfonic acid (10 mg) in benzene (5 mL) was heated at 55 °C for 15 min, then washed with aqueous $NaHCO_3$ (5%, 3 × 10 mL), and evaporated to give **11** (100 mg, 100%).

**B.** Crude products **10** and **11** of the addition reaction of $Me_2CuLi$ to **7** were treated with $p$-toluenesulfonic acid as described above. Chromatography on silica gel (EtOAc–hexanes, 5:95) afforded **11** (91%): $^1$H NMR (300 MHz) $\delta$ 4.07 (2 H, q, $J$ = 7 Hz, Et), 2.90 (1 H, m, H5$\alpha$), 2.58 (1 H, m, $J_{1-2}$ = 14 and 7.2 Hz, $J_{1-8a}$ = 11.7 Hz, H1), 2.25 (1 H, d, $J_{1-8a}$ = 11.7 Hz, H8a), 2.22–1.15 (14 H, m including t at $\delta$ 1.20 with $J$ = 7 Hz for Et), 0.94 (3 H, s, Me); an $^1$H NOE enhancement was observed at $\delta$ 2.25 (H8a) upon irradiation at $\delta$ 0.94 (Me); $^{13}$C NMR $\delta$ 212.6, 174.2, 60.7, 60.6, 42.2, 37.9, 37.8, 30.9, 27.6, 27.1, 22.1, 19.9, 14.1; IR (neat) 1720 cm$^{-1}$. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.32; H, 9.36.

**(1$\alpha$,4a$\alpha$,8a$\alpha$)-1-Isopropenyl-4a-methyl-8-methylenedecahydronaphthalene (14,8,9-Epi-$\beta$-gorgonene).** Sodium hydride (96 mg, 4 mmol) was reacted with dry DMSO (3 mL) at 70 °C until evolution of hydrogen ceased (1 h). The solution was cooled to 15 °C and treated with a solution of methyltriphenylphosphonium bromide (1.428 g, 4 mmol) in DMSO (3 mL). The mixture was stirred at 35 °C for 15 min, and the resultant red solution of the Wittig reagent was treated with **11** (300 mg, 1.26 mmol) in DMSO (1 mL), and then stirred at 40 °C for 10 h. Quenching with water (10 mL) at 10 °C was followed by extraction with pentane (4 × 25 mL) and then chromatography on silica gel (AcOEt–pentane, 2:98) to afford methylene ester **12** (158 mg, 53%): $^1$H NMR (60 MHz) $\delta$ 4.68 (2 H, m), 4.10 (2 H, q, $J$ = 7 Hz), 2.75 (1 H, m), 2.07 (4 H, m), 1.58 (9 H, m), 1.08 (3 H, t, $J$ = 7 Hz), 0.92 (3 H, s); HRMS calcd for $C_{15}H_{24}O_2$ $m/e$ 236.1777, found $m/e$ 236.1780.

A solution of **12** (120 mg, 0.51 mmol) in ether (5 mL) was treated with methyllithium in ether (1.5 M, 1 mL, 1.5 mmol) at 0 °C for 5 min, and the mixture was stirred at 0 °C for an additional 15 min. Quenching with water (5 mL) was followed by extraction with pentane (3 × 25 mL) to give tertiary alcohol **13** (113 mg, 100%): HRMS calcd for $C_{15}H_{24}$ ($M^+ - H_2O$) $m/e$ 204.1879, found 204.1882; HRMS calcd for $C_{14}H_{21}$ ($M^+ - H_2O - CH_3$) $m/e$ 189.1644, found 189.1642.

Freshly distilled thionyl chloride (0.24 mL) was added dropwise to a stirred solution of **13** (100 mg, 0.45 mmol) in dry pyridine (4 mL) at −15 °C. The mixture was stirred at 0 °C for 1 h, then poured (via syringe) onto ice, and extracted with pentane. Removal of pyridine from the extract by washing with hydrochloric acid (2 N) was followed by chromatography on silica gel (pentane) to give **14** (72 mg, 78%) as a colorless oil: $^1$H NMR (300 MHz) $\delta$ 4.67 (1 H, m, C8=CH$_2$), 4.61 (2 H, br s, C1C=CH$_2$), 4.51 (1 H, m, C8=CH$_2$), 2.46 (1 H, 3 d, $J_{1-2}$ = 3.3 and 11.7 Hz, $J_{1-8a}$ = 11.7 Hz, H1), 2.15–1.90 (3 H, m), 1.80 (1 H, d, $J_{1-8a}$ = 11.7 Hz, H8a), 1.70–1.16 (11 H, m including s at $\delta$ 1.60 for C1CMe), 1.00–0.90 (1 H, m), 0.90 (3 H, s, C4aMe); an $^1$H NOE enhancement (10%) was observed at $\delta$ 1.80 (H8a) but not at $\delta$ 2.46 (H1) upon irradiation at $\delta$ 0.90 (C4aMe), irradiation at $\delta$ 1.80 gave no NOE signal at $\delta$ 2.46; $^{13}$C NMR $\delta$ 149.0, 148.9, 110.1, 109.4, 55.1, 45.3, 40.8, 34.7, 32.4, 30.4, 30.3, 28.6, 23.5, 21.7, 18.0. Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.03; H, 11.88.

**Acknowledgment.** We thank the Instrument Program, Chemistry Division, National Science Foundation for financial assistance toward the purchase of the 300-MHz spectrometer.

**Registry No.** (±)-**1a**, 90545-43-0; (±)-**1b**, 112400-22-3; (±)-**2**, 112400-19-8; (±)-**3**, 112400-20-1; (±)-**4**, 112400-21-2; **5a**, 112400-23-4; **5b**, 112400-26-7; **6a**, 112421-60-0; **6b**, 112400-27-8; (±)-**7**, 112400-25-6; (±)-**8**, 112400-24-5; (±)-**9**, 112400-28-9; (±)-**10**, 112400-30-3; (±)-**11**, 112400-29-0; (±)-**12**, 112400-31-4; (±)-**13**, 112400-32-5; (±)-**14**, 51260-30-1; ClCOCH=CH$_2$, 814-68-6; (*E*)-HO$_2$CCH=CHSO$_2$Ph, 711-29-5; (*E*)-ClCOCH=CHSO$_2$Ph, 112421-59-7; EtO$_2$CCH=CH$_2$, 140-88-5; Ph$_3$PMe$^+$Br$^-$, 1779-49-3.

## Convenient Preparation of 11*H*-Benzo[*a*]fluorenone and 11*H*-Benzo[*b*]fluorenone

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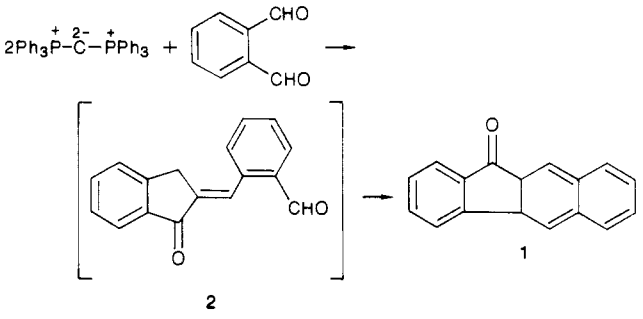
*Received March 5, 1987*

Benzofluorenones and their corresponding hydrocarbons have achieved recent significance because of their widespread occurrence in particulate matter from combustion of organic materials.[1] The hydrocarbons are useful as indicators in the determination of carbon acidities.[2] Commercial availability of the hydrocarbons has been variable and such samples have sometimes been impure but alternative syntheses have generally been rather lengthy. Thus, we were struck by Bestmann's report that 11*H*-benzo[*b*]fluorenone (**1**) is produced by the reaction of hexaphenylcarbodiphosphorane with phthalaldehyde.[3] On working out a possible mechanism for this reaction during a research group meeting it appeared that **2** is a reasonable intermediate in this reaction. **2** should also




be available even more readily from the chalcone condensation of 1-indanone with phthalaldehyde. In the ev-

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