Tetrahedron Vol 49, No 11, pp 2145-2150, 1993
Printed in Great Britain

0040-4020/93 $6 00+ 00

Stereoselective Formation of 1,4-Dialkoxy-1,3-Dienes from Propargyl Ethers and Molybdenum Carbene Complexes

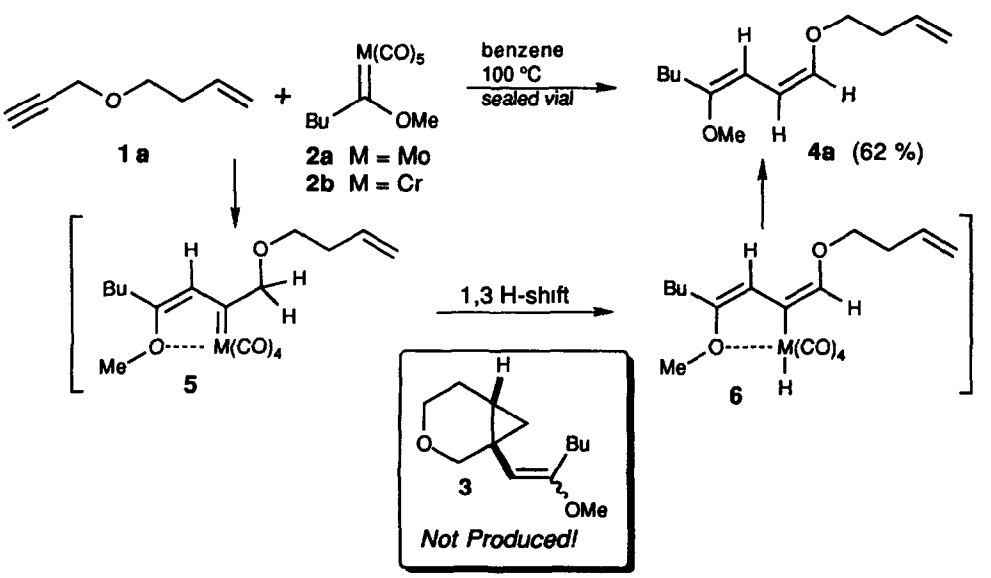
Daniel F. Harvey* and David A. Neil

Department of Chemistry - 0506
University of California at San Diego
La Jolla, CA 92093-0506

(*Received in USA* 14 *October* 1992)

Abstract: Under mild conditions, 1,4-dialkoxy-1,3-butadienes can be smoothly prepared with a high level of stereoselectivity by thermolysis of molybdenum carbene complexes in the presence of propargyl ethers

Recently we have described the reactivity of 1,6- and 1,7-enynes with Fischer carbene complexes [1] When appropriate substituents are present, bicyclo[3 1.0]hexane and bicyclo[4.1 0]heptane ring systems can be produced in good yield While studying the effect of various functionality on the outcome of this metal-mediated cyclization process, the reactivity of ether **1a** with molybdenum carbene complex **2a** was investigated with the

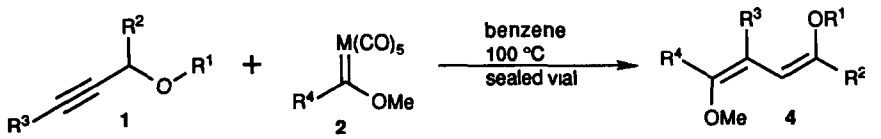


Scheme 1

expectation that 3-oxabicyclo[4.1.0]octane **3** would be produced. However, instead of the desired cyclopropanation product, 1,4-dialkoxy-1,3-butadiene **4a** was obtained in 62% yield as a single geometric isomer Since this represents a useful method for the stereoselective preparation of 1,4-dialkoxy-1,3-butadienes we have investigated the generality of this process These studies are described herein

In Table 1 are representative examples which serve to define the general scope of this reaction. This process only proceeds smoothly with molybdenum carbene complexes The analogous chromium complex, **2b**, produced **4** in only low yield (entries 2 and 4). Both alkyl and silyl substituents can be tolerated at R^1 Replacement of H with Me at the R^3 position was problematic, producing the expected 1,3-butadiene **4d** in only 13% yield. The low efficiency with this substrate is probably due to the absence of regioselectivity in the formation of vinylcarbene intermediate **5** (vide infra) Replacement of H with Me at the R^2 position resulted in no erosion of yield or stereoselectivity. The butyl group of the carbene complex can be replaced by a phenyl substituent (entry 8) without dramatically altering the overall efficacy of the reaction

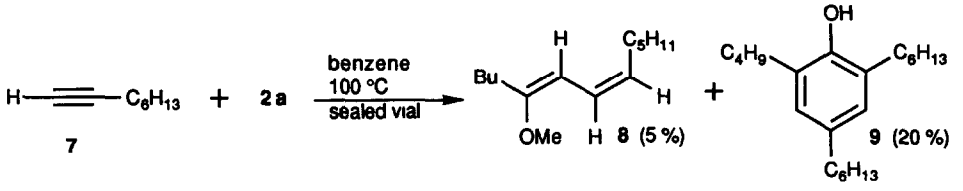
Table 1



	Substrate	R1	R2	R3	R4	M	4 (%)
1	**a**	4-butenyl	H	H	butyl	Mo	62
2	**a**	4-butenyl	H	H	butyl	Cr	< 5
3	**b**	butyl	H	H	butyl	Mo	51
4	**b**	butyl	H	H	butyl	Cr	<5
5	**c**	TBDMS	H	H	butyl	Mo	77
6	**d**	TBDMS	H	Me	butyl	Mo	13
7	**e**	TBDMS	Me	H	butyl	Mo	77
8	**f**	TBDMS	H	H	Ph	Mo	66

The mechanism for this reaction is believed to be as outlined in Scheme 1 Loss of carbon monoxide and reaction of the resulting coordinatively unsaturated carbene complex with the alkyne unit of **1** leads to vinylcarbene intermediate **5** Subsequent 1,3-hydrogen shift gives vinylhydride intermediate **6** which, after reductive elimination, leads to 1,3-diene **4**

This reaction was found to proceed smoothly only when the propargylic oxygen was present Treatment of molybdenum carbene complex **2a** with 1-octyne (**7**) under the same conditions led to the formation of



methoxybutadiene **8** in only 5 % yield, along with phenol **9** in 20 % yield. The alkoxy substituent increases the acidity of the α-hydrogens, thus facilitating the 1,3-hydrogen shift step from carbene complex **5** to vinylhydride intermediate **6** Phenol **9** results from the reaction of in situ generated carbene complex **5** with a second equivalent of alkyne, followed by CO insertion, electrocyclic ring closure, in situ reduction and elimination Such a process has previously been observed in related studies of reactions of molybdenum[1b] and chromium carbene complexes.[2]

Several related carbene-based enol ether formation reactions have previously been reported. Fischer and co-workers have described the base catalyzed conversion of chromium carbene complexes to enol ethers.[3,4] The mechanism for this reaction has been suggested to involve a base catalyzed 1,3-hydrogen shift to give a metal hydride intermediate which reductively eliminates to produce the enol ether The mechanism proposed for the conversion of **5** to **4** is analogous to this pathway [5]

Tungsten carbene complexes have previously been shown to react with alkynes to give substituted 2-alkoxy-1,3-butadienes [6] Though alternative pathways for this reaction have been considered,[6a] it may be viewed as a 1,5-hydrogen shift from a vinylcarbene intermediate to give a vinylhydride complex, which upon reductive elimination produces the alkoxybutadiene product Katz and Yang have recently reported the preparation of a 1,3-diene derived product from the reaction of a chromium carbene complex with 1-heptene-6-yne that is likely to have been formed via a similar 1,5-hydrogen shift pathway [7] These examples differ significantly from those described herein as they involve a 1,5- rather than a 1,3-hydrogen shift pathway from a vinylcarbene intermediate

Several factors are believed to be responsible for the high stereoselectivity of this process Initial reaction of the carbene complex with the alkyne can lead to either the E- or Z-isomer of vinylcarbene intermediate **6** Equilibration between the E- and Z-isomers may occur, with only the Z-isomer going on to product.[8] Alternatively, formation of the Z-isomer may be preferred because of the ability of the enol ether oxygen to coordinate to the metal, resulting in the formation of 18-e$^-$ complexes **5** and **6** The corresponding E-isomer cannot internally stabilize these reactive intermediates by oxygen coordination

The high stereoselectivity at the 3,4-position is thought to arise from the stereoselective formation of vinylhydride complex **6** A severe steric interaction between the $M(CO)_4H$ group and the alkoxy substituent ($O(CH_2)_2CH{=}CH_2$) would be present in the alternative stereoisomer Similar mechanistic rationales have been invoked to account for the stereoselective formation of enol ethers and enol acetates from Fischer carbene complexes [3-5] However, as noted in Table I, replacement of H with Me at this position (entry 7) does not hinder the reaction or decrease the stereoselectivity, suggesting that electronic factors may also be influencing this process

Experimental

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 500 MHz or G E 300 MHz spectrometer IR spectra were recorded on a Mattson Galaxy 2020 FT-IR spectrophotometer Low resolution mass spectra were recorded on a Hewlett-Packard 5970 mass-selective detector (20 eV) interfaced with a Hewlett-Packard 5890 gas chromatograph equipped with a 12 m x 0 2 mm HP-1 fused silica capillary column High resolution mass spectra were performed at the University of California at Riverside Mass Spectrometry Facility on a VG-ZABZFHF or VG-7070EHF mass spectrometer Column chromatography was performed with Fischer Scientific florisil (100-200 mesh) or silica gel (200-425 mesh) All reagents were obtained from commercial suppliers and used as received unless otherwise indicated Except as noted below, reactions were

performed under a nitrogen atmosphere in flame-dried glassware. Benzene, THF, and Et_2O were distilled from benzophenone ketyl under a nitrogen atmosphere. Methylene chloride was distilled from CaH_2 under a nitrogen atmosphere. Compounds **1a** and **4a** were prepared as described in reference 1b Because of decomposition during transport, we were unable to obtain satisfactory combustion analysis for the 1,4-dialkoxy-1,3-butadienes Except as noted below, dienes **4** were determined to be >98% pure by ^1H NMR spectroscopy.

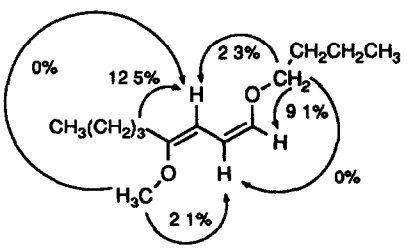
General procedure. A solution of the propargyl ether and the carbene complex in benzene (22 mL) was heated at 100 °C behind a blast shield in a glass vial sealed with a rubber lined screw cap and aluminum foil After cooling to room temperature, the crude reaction mixture was directly concentrated in vacuo and chromatographed on florisil to give the 1,3-diene product.

Preparation of butyl ether 1b. To a suspension of NaH (0.400 g of a 80% dispersion in oil, washed with hexanes, 13 3 mmol) in Et_2O (65 mL) containing HMPA (2.4 mL) at room temperature was added 1-butanol (0 75 mL, 8.7 mmol). After heating at reflux for 3 h, the reaction mixture was cooled to room temperature and treated with propargyl bromide (1.30 mL, 80 wt. % in toluene, 11 5 mmol) After 4 h at room temperature, the reaction mixture was quenched with saturated $NaHCO_3$ solution (10 mL) and the organic layer was extracted with H_2O (3 x 15 mL), dried over $MgSO_4$, filtered, concentrated in vacuo and chromatographed on silica gel to give **1b** (1 03 g, 84 %)

1b: ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7 3 Hz, 3 H), 1 38 (sextet, J = 7.3 Hz, 2 H), 1 58 (p, J = 6 8 Hz, 2 H), 2.41 (t, J = 2 4 Hz, 1 H), 3 51 (t, J = 6.8 Hz, 2 H), 4.13 (d, J = 2 4 Hz, 2 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 19 2, 31 5, 57 9, 69 9, 74.0, 80 0; IR (CH_2Cl_2) 3303, 29612, 2935, 2874, 2118 (very weak), 1466, 1459 cm^{-1}; MS (EI, 20 eV) *m/e* 111 (M^+ - H, 1), HRMS for $C_7H_{11}O$ calcd 111.0810, found 111.0812

(Z,Z)-1-butoxy-4-methoxy-1,3-octadiene (4b). Following the general procedure, ether **1b** (112 3 mg, 1 00 mmol) and complex **2a** (193 2 mg, 0 57 mmol) were heated for 1.25 h to give recovered **2a** (10 0 mg, 5 %) and **4b** (62.3 mg 51 %)

4b: ^1H NMR (500 MHz, C_6D_6) δ 0 76 (t, J = 7 3 Hz, 3 H), 0 78 (t, J = 7 3 Hz, 3 H), 1.20 (sextet, J = 7 3 Hz, 2 H), 1 24 (sextet, J = 7 3 Hz, 2 H), 1 38 (p, J = 7 6 Hz, 2 H), 1 40 (p, J = 7.0 Hz, 2 H), 2 04 (t, J = 7 3 Hz, 2 H), 3.32 (s, 3H), 3.44 (t, J = 6.3 Hz, 2 H), 5.75 (d, J = 6 3 Hz, 1 H), 5 81 (dd, J = 10.7, 6.3 Hz, 1 H), 6 01 (d, J = 11 2 Hz, 1 H), ^{13}C NMR (125 MHz, C_6D_6) δ 13 89 (q), 14 02 (q), 19 3 (t), 22 6 (t), 29.9 (t), 31 6 (t), 32 2 (t), 55.9 (q), 72 2 (t), 101 8 (d), 103 7 (d), 143 8 (d), 154 6 (s), IR (CH_2Cl_2) 2962, 2936, 2874, 1614, 1466 cm^{-1}; MS (EI, 20 eV) *m/e* 213 (MH^+, 14) 212 (M^+, 100), HRMS for $C_{13}H_{24}O_2$ calcd 212 1776, found 212.1777 Stereochemistry assigned by olefinic proton coupling constants and NOE difference spectroscopy as shown to the right



Preparation of silyl ether 1c. Propargyl alcohol (1 00 mL, 17 2 mmol) and triethylamine (2 6 mL, 19 mmol) were dissolved in CH_2Cl_2 (50 mL) at room temperature, cooled to 0 °C and treated with *t*-butyldimethylsilyl chloride (2 60 g, 18 7 mmol) The reaction mixture was allowed to warm to room temperature and stirred for 2 5 h The reaction mixture was then quenched with saturated $NaHCO_3$ solution (10 mL) and the organic layer extracted with H_2O (3 x 15 mL), dried over $MgSO_4$, filtered, concentrated in vacuo and chromatographed on florisil to give **1c** (2 22 g, 76 %).

1c ^1H NMR (500 MHz, $CDCl_3$) δ 0 12 (s, 6 H), 0 90 (s, 9 H), 2 38 (t, J = 2 4 Hz, 1 H), 4 30 (d, J = 2 4 Hz, 2 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.2, 18 2, 25 8, 51 5, 72.8, 82 4, IR (CH_2Cl_2) 3303, 2957, 2932, 2897, 2886, 2858, 2122 (very weak), 1473, 1464 cm^{-1}; MS (EI, 20 eV) *m/e* 170 (M^+, 2), HRMS for $C_9H_{18}OSi$ calcd 170 1127, found 170 1125

(Z,Z)-1-*t*-Butyldimethylsiloxy-4-methoxy-1,3-octadiene (4c). Following the general procedure, ether **1c** (90.0 mg, 0 53 mmol) and **2a** (101 5 mg, 0 30 mmol) were heated for 1 5 h to give of **4c** (63 3 mg, 77 %) and $Mo(CO)_6$ (25 mg, 31 %)

4c ^{1}H NMR (500 MHz, C_6D_6) δ 0.05 (s, 6 H), 0 80 (t, J = 7 3 Hz, 3 H), 0.94 (s, 9 H), 1 22 (sextet, J = 7.3 Hz, 2 H), 1.41 (p, J = 7.3 Hz, 2 H), 2.06 (t, J = 7.3 Hz, 2 H), 3.31 (s, 3 H), 5 95 (dd, J = 11.2, 5.9 Hz, 1 H), 6 01 (d, J = 11.2 Hz, 1 H), 6 12 (d, J = 5 9 Hz, 1 H), ^{13}C NMR (125 MHz, C_6D_6) δ -5.3, 14.0, 18 5, 22.5, 25 8, 29 8, 31.7, 55.9, 103 3, 106.1, 137.2, 154.9; IR (CH_2Cl_2) 2958, 2933, 2899, 2885, 2859, 1608, 1472, 1464 cm^{-1}; MS (EI, 20 eV) *m/e* 270 (M^+, 23); HRMS for $C_{15}H_{30}O_2Si$ calcd 270 2015, found 270 2001 Stereochemistry assigned by proton coupling constants, NOE difference spectroscopy and comparison with compound **4b**. For example, irradiation of the methylene signal at δ 2.06 produced a 7 8 % enhancement of the olefin signal at δ 6.01.

(Z,Z)-1-*t*-Butyldimethylsiloxy-4-methoxy-4-phenyl-1,3-octadiene (4f). Following the general procedure, ether **1c** (131.8 mg, 0.77 mmol) and pentacarbonyl(phenylmethoxycarbene)molybdenum (0) (164 8 mg, 0 46 mmol) were heated for 1.5 h to give **4f** (88 mg, 66 %)

4f ^{1}H NMR (500 MHz, C_6D_6) δ 0.02 (s, 6 H), 0 90 (s, 9 H), 3 41 (s, 3 H), 6 03 (dd, J = 11.2, 5 9 Hz, 1 H), 6 24 (dd, J = 5 9, 1.0 Hz, 1 H), 6 87 (dd, J = 11 2, 1 0 Hz, 1 H), 7 00 (t, J = 7 3 Hz, 1 H), 7 09 (t, J = 7 3 Hz, 2 H), 7 57 (d, J = 7 3 Hz, 2 H), ^{13}C NMR (125 MHz, C_6D_6) δ -5 4, 18 5, 25.7, 58.7, 106.2, 107 7, 126 0, 128 7, 136 6, 140 3, 153 8; IR (CH_2Cl_2) 2957, 2933, 2897, 2886, 2858, 1635, 1594, 1575, 1490, 1472, 1464, 1450 cm^{-1}, MS (EI, 20 eV) *m/e* 290 (M^+, 15), HRMS for $C_{17}H_{26}O_2Si$ calcd 290 1702, found 290 1709. Stereochemistry assigned by proton coupling constants, NOE difference spectroscopy and comparison with compound **4b**. For example, irradiation of the methoxy signal at δ 3 31 produced a 3 9 % enhancement of the olefin signal at δ 6.03

Preparation of silyl ether 1d. To a solution of 2-butyn-1-ol (1 00 mL, 13.4 mmol) and triethylamine (2.0 mL, 14 mmol) in CH_2Cl_2 (60 mL) at room temperature was added *t*-butyldimethylsilyl chloride (2 02 g, 13.4 mmol) After heating at reflux for 6 h, the reaction was cooled to room temperature and quenched with saturated $NaHCO_3$ solution (15 mL) and the organic layer extracted with H_2O (2 x 20 mL), dried over $MgSO_4$, filtered, concentrated in vacuo and chromatographed on florisil to give **1d** (2 22 g, 90 %)

1d ^{1}H NMR (500 MHz, $CDCl_3$) δ 0 10 (s, 6 H), 0 90 (s, 9 H), 1 82 (t, J = 2.4 Hz, 3 H), 4.26 (q, J = 2.4 Hz, 2 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ -5 2, 3 6, 18 3, 25 9, 51 9, 77 7, 80 8, IR (CH_2Cl_2) 2957, 2931, 2897, 2885, 2858, 2236 (very weak), 1472, 1464 cm^{-1}, MS (CI, NH_3) *m/e* 202 (MNH_4^+, 6), 185 (MH^+, 57), HRMS for $C_{10}H_{21}OSi$ calcd 185 1362, found 185 1364

(Z,Z)-1-*t*-butyldimethylsiloxy-4-methoxy-3-methyl-1,3-octadiene (4d). Following the general procedure, ether **1d** (108 5 mg, 0 59 mmol) and **2a** (109 3 mg, 0.32 mmol) were heated for 1.5 h to give recovered **2a** (10 0 mg, 9 %) and 12 mg (< 13 %) of crude **4d** which proved to be very unstable, undergoing decomposition upon isolation and characterization

4d ^{1}H NMR (500 MHz, C_6D_6) δ 0 02 (s, 6 H), 0 85 (t, J = 7 3 Hz, 3 H), 0 92 (s, 9 H), 1 28 (sextet, J = 7 3 Hz, 2 H), 1 47 (p, J = 7 3 Hz, 2 H), 2 18 (t, J = 7 3 Hz, 2 H), 2 23 (s, 3 H), 3 32 (s, 3 H), 5 90 (d, J = 6 8 Hz, 1 H), 6 12 (d, J = 6 3 Hz, 1 H).

Preparation of silyl ether 1e. To a solution of 3-butyn-2-ol (200 μL, 2 55 mmol) in CH_2Cl_2 (35 mL) at room temperature were added imidazole (204 mg, 3 00 mmol) and *t*-butyldimethylsilyl chloride (409 mg, 2 71 mmol) The solution was heated at reflux for 24 h After cooling to room temperature, the reaction mixture was quenched with a saturated $NaHCO_3$ solution (5 mL) and the organic layer was extracted with H_2O (2 x 10 mL), dried over $MgSO_4$, filtered, concentrated in vacuo and chromatographed on florisil to give **1e** (410 mg, 87 %).

1e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0 12 (s, 3 H), 0 13 (s, 3 H), 0 90 (s, 9 H), 1 42 (d, J = 6 4 Hz, 3 H), 2 37 (d, J = 2 5 Hz, 1 H), 4.51 (qd, J = 6 4, 2 0 Hz, 1 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ -5 0, -4.7, 18 2, 25 3, 25 8, 58 8, 71 1, 86 4, IR (CH_2Cl_2) 3303, 2986, 2957, 2932, 2886, 2857, 2114 (very weak), 1473, 1464, 1444 cm^{-1}, MS (EI, 20 eV) *m/e* 184 (M^+, 0 4),

(Z,Z)-1-*t*-butyldimethylsiloxy-4-methoxy-2,4-nonadiene (4e). Following the general procedure, ether **1e** (104 4 mg, 0.57 mmol) and **2a** (113.3 mg, 0 34 mmol) were heated for 1.5 h to give **4e** (73 5 mg, 77 %) and $Mo(CO)_6$ (40 mg, 45 %)

4e· ^{1}H NMR (300 MHz, C_6D_6) δ 0.13 (s, 6 H), 0 85 (t, J = 7 3 Hz, 3 H), 1 02 (s, 9 H), 1 27 (sextet, J = 7.3 Hz, 2 H), 1.46 (p, J = 7.4 Hz, 2 H), 1.76 (s, 3 H), 2 11 (t, J = 7.4 Hz, 2 H), 3 33 (s, 3 H), 5.83 (d, J = 10 8 Hz, 1 H), 5 92 (d, J = 10.7 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ -3.7, 14.1, 18.5, 22.5, 23 2, 26 0, 29 8, 31 6, 56.0, 105.0, 105.3, 146.0, 153 5, IR (CH_2Cl_2) 2959, 2933, 2899, 2886, 2859, 1622, 1473, 1464, 1379, 1296, 1282, 1253, 1186, 1150, 1136, 1006 cm^{-1}, MS (EI, 20 eV) *m/e* 284 (M^+, 51), 269 (31), 241 (24), 169 (13), 127 (12), 115 (13), 111 (10), 95 (13), 89 (40), 85 (12), 75 (24), 73 (100), 59 (16), 57 (29), 43 (15), 41 (26), HRMS for $C_{16}H_{32}O_2Si$ calcd 284.2172, found 284 2161

(Z,Z)-4-methoxy-5,7-tridecadiene (8) and 2-butyl-4,6-dihexyl-phenol (9): Following the general procedure, 1-octyne (**7**, 120 4 mg, 1.09 mmol) and complex **2a** (207.2 mg, 0 62 mmol) were heated for 1 h to give recovered **2a** (10.0 mg, 5 %), diene **8** (6 5 mg, 5 %, ^{1}H NMR indicated that small amounts of other diene isomers were also present. Spectral data for the major isomer is provided below) and phenol **8** (40 2 mg, 20 %)

8 ^{1}H NMR (500 MHz, C_6D_6) δ 0.82 (t, J = 7 3 Hz, 3 H), 0 86 (t, J = 7 3 Hz, 3 H), 1.20-1 30 (m, 6 H), 1 36-1 42 (m, 4 H), 2.03 (t, J = 7 3 Hz, 2 H), 2 21 (q, J = 7 3 Hz, 2 H), 3.27 (s, 3 H), 5 39 (dt, J = 11 2, 7.3 Hz, 1 H), 5 64 (d, J = 11 2 Hz, 1H), 6 81 (t, J = 11 2 Hz, 1 H), IR (C_6D_6) 2958, 2931, 2873, 2862, 2854, 1652, 1467 cm^{-1}; MS (EI, 20 eV) *m/e* 211 (MH^+, 5), 210 (M^+, 32), HRMS for $C_{14}H_{26}O$ calcd 210 1984, found 210.1987. The stereochemistry of **8** was assigned by proton coupling constants, NOE difference spectroscopy and comparison with compound **4b** For example, irradiation of the methylene signal at δ 2 21 produced a 5 8 % enhancement of the olefin signal at δ 5 64.

9. ^{1}H NMR (500 MHz, C_6D_6) δ 0 85-0 90 (m, 9 H), 1 21-1 36 (m, 14 H), 1 53-1 66 (m, 6 H), 2 50 (apparent quartet, J = 8 Hz, 4 H), 2.55 (t, J = 7 8 Hz, 2 H), 4 19 (s, 1 H, exchanges with D_2O), 6 85-6 87 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13 98, 14 09, 22 62, 22 72, 29 1, 29 3, 29 9, 30 0, 30 3, 31 73, 31 75, 31.85, 32 1, 35 3, 127 44, 127 46, 127 67, 127 71, 134 5, 149 2, IR (CH_2Cl_2) 3603, 2958, 2930, 2872, 2857, 1477, 1468 cm^{-1}, MS (EI, 20 eV) *m/e* 319 (MH^+, 20), 318 (M^+, 82), HRMS for $C_{22}H_{38}O$ calcd 318 2923, found 318 2923

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