ygen quenching, electrochemical evidence, and our rough correlation of potentials with reactivity of substrates lend strong support to our proposed SET mechanism.

We are continuing to evaluate reagents of this type to determine the scope of functional groups reduced and their E_{red} limit as well as the E_{ox} limit of other aryl enediol dianions.

Experimental Section

General. Benzoin (2) and chalcone (14) (Aldrich) were recrystallized from EtOH before use. DMSO was distilled from CaH_2 at reduced pressure (~20 mm) and stored under N_2, NaOH was ground to a fine powder just before use. NaH was weighed as a 56% suspension in mineral oil. It was necessary to wash the oil from the NaH powder in the reaction flask or reactions usually did not proceed. The wash was performed with petroleum ether under N_2. After standing for a short time, the solvent wash could be easily decanted. Reactions were stopped, and the DMSO was removed by pouring the solution into several hundred mL of acidified water (HCl) and extracting into Et_2O, which was then washed with water. The DMSO-free ether extracts were further divided into A1 and N fractions by standard bicarbonate extraction procedures. Final ether extracts were dried with $CaCl_2$ or anhydrous Na_2SO_4. Fractions were usually analyzed by GC/MS (EI and CI-H_2 modes) or by HPLC/PB/MS before recrystallization and/or preparative chromatography. GC employed a HP-1 (0.2 mm i.d. × 12.5 m and 0.33 μm film, $\beta = 150$) capillary column. HPLC used a 5-μm Resolve C18 column with MeOH/H_2O solvents. Preparative plate chromatography was done on 20 × 20 cm silica gel 60 (PLK-F254) plates. Suitable spectra (IR, NMR, MS) were obtained to match literature data for all known compounds. Melting points were taken in capillary tubes and are reported uncorrected in degrees C. A few representative procedures are included.

(*Z*)-α,β-Dibenzoylstyrene (1), Benzoin (2), and NaOH. 1 (1.56 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were dissolved in 25 mL of DMSO. NaOH (0.61 g, 15.0 mmol) was added and the mixture stirred at rt for 2 h. The neutral layer gave on evaporation nearly pure 1,2,4-triphenyl-1,4-butanedione (3, 1.59 g, ~100%) of mp 119–125.5 °C. The mp was suppressed by the presence of a small amount of yellow benzil (8). One recrystallization from EtOH gave 1.45 g (91%) of colorless 3: mp 124.5–126 °C (lit.[2] mp 126 °C). The A1 fraction eventually gave 1.05 g (91.4%) of crude benzilic acid (4), mp 139.5–146 °C (and mp 146.5–148.5 °C from hexane/acetone). In a duplicate reaction, which was allowed to proceed only 15 min, a small quantity of each, benzil (8) and benzoin (2), were isolated.

Chalcone (14), 2, and NaOH. 14 (4.16 g, 20.0 mmol) and 2 (2.12 g, 10.0 mmol) were dissolved in DMSO (50 mL) containing NaOH (11.2 mmol) prepared in situ by NaH/oil (0.48 g) and distilled water (0.32 g, 17.8 mmol). After being stirred for 4 h under N_2 atmosphere, the dark green solution was worked up as usual. Evaporation of the neutral layer and drying in a vacuum desiccator afforded a very viscous oil (4.12 g), part of which (1.57 g) was placed on a column of alumina (60 mL Alcoa F-20) and developed with petroleum ether. Elution with 2% Et_2O in petroleum ether afforded 5-benzoyl-1,3,4-triphenylcyclopent-1-ene (15) (0.31 g, 20.3%), mp 177–179 °C (lit.[12d] mp 181–182 °C). Continued elution afforded 2-benzoyl-1,3,4-triphenylcyclopent-1-ene (16, 0.34 g, 22.3%), mp 121–122 °C (lit.[12a] mp 123 °C).

The A1 fraction gave a crude acid product (1.24 g, 54.4%) that was recrystallized from acetone/hexane to give 4: mp 138–140 °C.

A similar reaction of 14 and 2 with powdered NaOH was conducted with a 1:1:3 mole ratio for 4 h (green). Analysis by GC/MS gave 15 (71.6%, mixture of 3 isomers) and 16 (27.7%, mixture of 2 isomers). About 0.7% of 14 remained. As expected, 1 equiv of 2 and a small amount of 8 were returned. No higher molecular weight oligomers were detected under these conditions. The A1 layer represented a 94.3% conversion of the theoretical (1 equiv).

The ratio of 15 to 16 was reversed (28:69) when the reaction was conducted with a 1:1:4:2 mole ratio of 14 and 2 with NaH and water for 6 h (red). About 3% of 14 was returned in this reaction.

Nitrobenzene (17), 2, and NaOH. 17 (0.369 g, 3.0 mmol) and 2 (1.908 g, 9.0 mmol) were dissolved in 25 mL of DMSO with NaOH (1.08 g, 27.0 mmol) and stirred for 5 h. The blue solution became dark orange within 1 h. Analysis of the neutral indicated a 42.4% yield of *N*-benzoylaniline (18), a sizeable amount of deoxybenzoin, and other compounds. PLC isolated 215 mg (36.4%) of 18, mp 162.5–163.5 °C (cyclohexane). No starting material, 17, was returned.

The original acidified water was made basic and extracted with ether. The ether was dried with Na_2SO_4 and evaporated to afford 140 mg of a yellow oil. GC/MS and FTIR analysis showed this oil to consist of mainly azoxybenzene (20, 102 mg, 0.515 mmol) and aniline (19, 18.8 mg, 0.2 mmol). These amounts correspond to yields of 34% and 6.7%, respectively.

9-Benzalfluorene (21), 2, and NaOH. 21 (1.27 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were dissolved in 25 mL of DMSO. NaOH (0.50 g, 12.5 mmol) was added and stirred for 6.5 h before workup (dark green). LC and GC/MS analysis of the neutral layer showed about 8.5% conversion of 21 to 9-benzylfluorene (22). Fractional recrystallization (EtOH) of a similar reaction gave 22; 5.1% of mp 132.5–134.5 °C (lit.[19] mp 134–5 °C).

9-Benzalfluorene (21), 2, NaOH, and H_2O. NaH (0.750 g of 80% in oil, 25.0 mmol) was washed under N_2 with hexanes. DMSO containing H_2O (0.270 g, 15.0 mmol) was added and stirred until the evolution of hydrogen began to subside. 21 (1.27 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were added with another 20 mL of DMSO and the mixture stirred for 6.5 h (dark red). Upon workup, it was necessary to filter a white precipitate that was poorly soluble in ether. This solid (0.713 g, 55.9%) was the crude hydrodimer 1,2-diphenyl-1,2-bis(9-fluorenyl)ethane (23), mp 305–315 °C (lit.[19] mp 310–313 or 319–320 °C). Recrystallization from anisole gave mp 310–313 °C (fast).

Concentration of the ether and trituration with $CHCl_3$ gave additional 23 (205 mg, 16.1%), mp 307–320 °C. LC and GC/MS analysis of the remains of the neutral layer indicated at 11.6% return of starting material and 5.9% of dihydro 22 in addition to another ~10% of 23.

The A1 layer weighed 536 mg (2.35 mmol), which closely agrees with the amount of reduction shown by 82% of dimer 23 (2.05 mmol) and 6% of 22 (0.3 mmol).

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Registry No. 1, 13249-75-7; 2, 119-53-9; 3, 4441-01-4; 4, 76-93-7; 8, 134-81-6; 14, 94-41-7; 15, 84709-76-2; 16, 84627-21-4; 17, 98-95-3; 18, 93-98-1; 19, 62-53-3; 20, 495-48-7; 21, 1836-87-9; 22, 1572-46-9; 23, 1772-27-6.

A New Three-Carbon Homologating Agent for Synthesis of γ-Keto Aldehydes

Xiyan Lu,* Cheng Guo, and Dawei Ma

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

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Homologation of aldehydes by three carbons is a process of considerable synthetic interest.[1,2] γ-Keto aldehydes are widely used in organic synthesis, especially as intermediates for the preparation of cyclopentenones.[3] A number of syntheses of γ-keto aldehydes with three-carbon homologating agents have been reported.[4-11] Most of these

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Scheme I

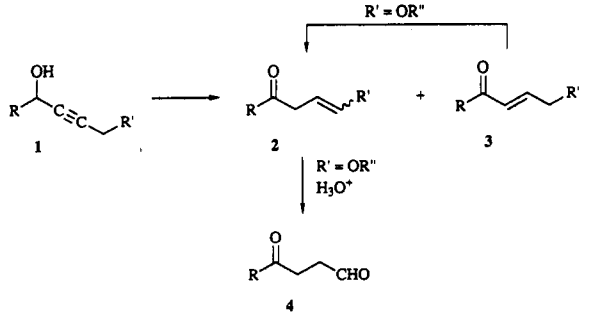


Table I. Isomerization of 1-Methoxy-2-alkyn-4-ols with $IrH_5[P(Pr\text{-}i)_3]_2$ Catalyst[a]

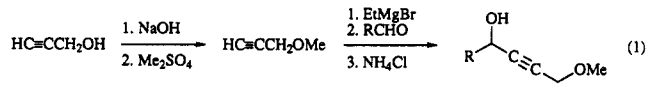
compd	R	cat. (mol %)	i-Pr_3P/cat.	time (h)	isolated yield (%)
1a	n-C_3H_7	2.5	0	60	68
1a	n-C_3H_7	2.0	4	61	72
1b	n-C_4H_9	2.0	0	60	60
1c	n-C_5H_{11}	5.0	0	18	67
1c	n-C_5H_{11}	2.0	4	61	69
1d	n-C_6H_{13}	2.5	0	62	66
1d	n-C_6H_{13}	2.0	4	61	73

[a] Reaction conditions: 1, 2 mmol; toluene, 5 mL; 110 °C.

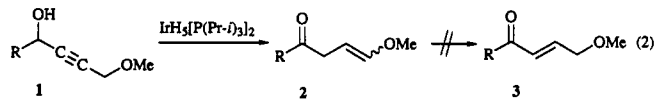
routes, however, require multistep preparation of a special reagent.

In our study of the isomerization of acetylenic compounds catalyzed by transition-metal complexes,[12a] we found that isomerization of a propargylic alcohol yields two products, an α,β-enone and a β,γ-enone.[12b] These products are in equilibrium, although the former is favored thermodynamically. It has been reported that α,β- and β,γ-enones equilibrate with a rather small free energy difference (ΔG = 1 kcal/mol at 25 °C),[13] which indicates that the two isomers can easily interconvert. On the other hand, allyl ethers isomerize smoothly to enol ethers under transition-metal complex catalysis.[14] It occurred to us that if the alkynol were substituted with an alkoxy group, the stabilizing effect of conjugation in the resulting enol ether should make the β,γ-enone the major product, which could be easily turned into a γ-keto aldehyde on hydrolysis (Scheme I).

Starting from propargyl alcohol, we prepared 1-methoxy-2-alkyn-4-ols 1 (eq 1).



Studies of the isomerization of 1 catalyzed by $IrH_5[P(Pr\text{-}i)_3]_2$ showed that the only product was β,γ-enone **2** (eq 2). No α,β-enone **3** was detected. The results are summarized in Table I.



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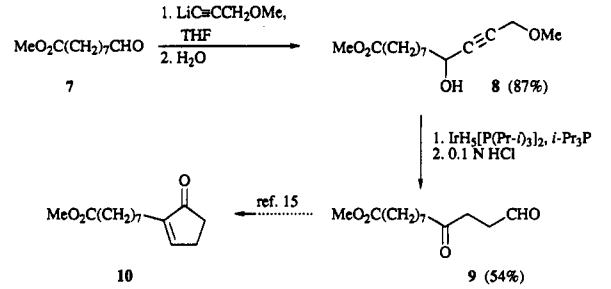
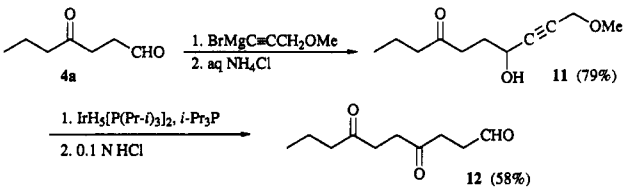
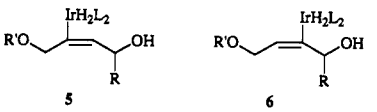
Scheme II



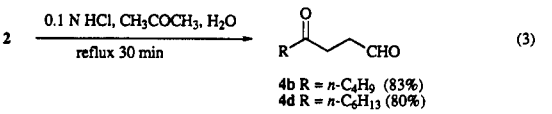
Scheme III



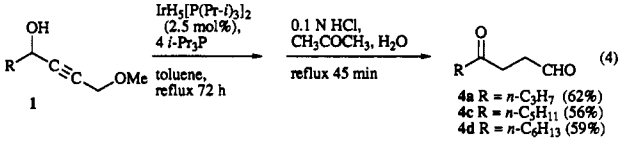
The mechanism of the reaction may be similar to that of the isomerization of propargylic alcohols catalyzed by iridium complexes.[12] The $IrH_5[P(Pr\text{-}i)_3]_2$ complex first loses two hydrogens to form the reactive species $IrH_3[P(Pr\text{-}i)_3]_2$, which coordinates with the triple bond. The insertion of the triple bond into the Ir–H bond may occur to form **5** and **6**. β-Hydrogen elimination from **5** may produce an allenic alcohol, which through addition and elimination of iridium hydride will generate the β,γ-enone **2**. On the other hand, β-hydrogen elimination from **6** could give α,β-enone **3**, which could isomerize to **2** as allyl ether isomerizes to an enol ether.



β,γ-Enones **2** can be hydrolyzed easily to γ-keto aldehydes **4** (eq 3).



The isomerization product of **1** can be hydrolyzed directly to **4** without isolation, thus providing a one-pot synthesis of **4**.



Methyl 9-oxononanoate (**7**), prepared by ozonolysis of methyl oleate, was homologated to ynol ester **8**, which was rearranged to keto aldehyde **9** in 47% overall yield (Scheme II). The conversion of **9** into cyclopentenone **10**, an intermediate for prostaglandin synthesis, has been reported.[15]

We also converted **4a** into diketo aldehyde **12** in 46% overall yield (Scheme III), thus demonstrating the utility of methyl propargyl ether as a building block for synthesis

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of polycarbonyl compounds.

Experimental Section

All isomerization reactions were carried out under prepurified Ar. Toluene was distilled from sodium benzophenone ketyl under Ar. ^{1}H NMR spectra were recorded in CCl_4 at 60 MHz unless specified otherwise.

Materials. Complex $IrH_5[P(Pr\text{-}i)_3]_2$ was prepared according to the reported method.[16] 1-Methoxy-2-alkyn-4-ols were prepared by the reaction of an aldehyde with the acetylenic carbanion of methyl propargyl ether.[17]

1-Methoxy-2-heptyn-4-ol (1a): yield 86%; bp 57–59 °C (1 mmHg); IR (neat) 3375, 2200, 1100 cm^{-1}; ^{1}H NMR δ 0.9 (t, J = 6 Hz, 3 H), 1.5 (m, 4 H), 2.9 (m, 1 H), 3.3 (s, 3 H), 4.0 (s, 2 H), 4.2 (m, 1 H); MS m/z (rel intensity) 141 (M^+ – H, 2), 125 (13), 113 (22), 99 (90), 71 (100), 43 (89). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.20; H, 9.98.

1-Methoxy-2-octyn-4-ol (1b): yield 84%; bp 92–94 °C (1 mmHg); IR (neat) 3375, 2200, 1100 cm^{-1}; ^{1}H NMR δ 0.9 (br t, 3 H), 1.5 (m, 6 H), 2.8 (s, 1 H), 3.4 (s, 3 H), 4.1 (s, 2 H), 4.3 (m, 1 H); MS m/z (rel intensity) 155 (M^+ – H, 8), 139 (7), 123 (4), 109 (20), 99 (53), 97 (36), 69 (63), 57 (44), 41 (100); HRMS calcd exact mass for ($C_9H_{16}O_2$ – H^+) 155.1072, found 155.1113.

1-Methoxy-2-nonyn-4-ol (1c): yield 69%; bp 88–92 °C (1 mmHg); IR (neat) 3375, 2200, 1100 cm^{-1}; ^{1}H NMR δ 0.9 (br t, 3 H), 1.4 (m, 8 H), 2.6 (m, 1 H), 3.3 (s, 3 H), 4.1 (s, 2 H), 4.3 (m, 1 H); MS m/z (rel intensity) 169 (M^+ – H, 11), 153 (19), 139 (7), 99 (6), 70 (100); HRMS calcd exact mass for ($C_{10}H_{18}O_2$ – H^+) 169.1229, found 169.1230.

1-Methoxy-2-decyn-4-ol (1d): yield 88%; bp 120–124 °C (1 mmHg); IR (neat) 3375, 2200, 1100 cm^{-1}; ^{1}H NMR δ 1.0 (br t, 3 H), 1.6 (m, 10 H), 3.1 (m, 1 H), 3.5 (s, 3 H), 4.2 (s, 2 H), 4.4 (m, 1 H); MS m/z (rel intensity) 183 (M^+ – H, 3), 167 (1), 153 (2), 139 (14), 99 (59), 69 (59), 45 (46), 43 (100); HRMS calcd exact mass for ($C_{11}H_{20}O_2$ – H^+) 183.1385, found 183.1374.

General Procedure for the Isomerization of 1-Methoxy-2-alkyn-4-ols 1. A mixture of 1 (2 mmol), $IrH_5[P(Pr\text{-}i)_3]_2$ (0.05 mmol), and i-Pr_3P(0.2 mmol) was refluxed in toluene (5 mL) until TLC showed that the reaction was complete. After cooling the mixture, the solvent was removed under reduced pressure. The red residue was purified by Kugelrohr distillation under reduced pressure to give 2 as a colorless oil.

1-Methoxy-1-hepten-4-one (2a): ot 60 °C (5 mmHg); IR (neat) 1715, 1660, 1105 cm^{-1}; ^{1}H NMR δ 0.8 (t, J = 6 Hz, 3 H), 1.4 (m, 2 H), 2.3 (m, 2 H), 3.2 (br s, 3 H), 3.5 (d, J = 5 Hz, 2 H), 4.4 (m, 1 H), 6.0 (m, 1 H); MS m/z (rel intensity) 143 (M^+ + H, 41), 127 (22), 113 (15), 99 (28), 77 (99), 71 (62), 43 (87), 41 (100); HRMS calcd exact mass for $C_8H_{14}O_2$ 142.0994, found 142.0932.

1-Methoxy-1-octen-4-one (2b): ot 80 °C (2 mmHg); IR (neat) 1715, 1660, 1110 cm^{-1}; ^{1}H NMR δ 0.8 (t, J = 7 Hz, 3 H), 1.1–1.4 (m, 4 H), 2.2 (m, 2 H), 3.1 (s, 3 H), 3.4 (d, J = 5 Hz, 2 H), 4.4 (m, 1 H), 6.0 (m, 1 H); MS m/z (rel intensity) 156 (M^+, 5), 127 (7), 85 (41), 71 (50), 59 (100), 57 (79); HRMS calcd exact mass for $C_9H_{16}O_2$ 156.1150, found 156.1103.

1-Methoxy-1-nonen-4-one (2c): ot 80 °C (1 mmHg); IR (neat) 1715, 1660, 1105 cm^{-1}; ^{1}H NMR δ 0.9 (br t, 3 H), 1.1–1.4 (m, 6 H), 2.3 (m, 2 H), 3.2 (s, 3 H), 3.5 (d, J = 5 Hz, 2 H), 4.4 (m, 1 H), 6.0 (m, 1 H); MS m/z (rel intensity) 171 (M^+ + H, 38), 155 (7), 141 (20), 99 (39), 72 (100), 43 (76); HRMS calcd exact mass for $C_{10}H_{18}O_2$ 170.1307, found 170.1280.

1-Methoxy-1-decen-4-one (2d):[5] ot 100 °C (1 mmHg); IR (neat) 1715, 1660, 1110 cm^{-1}; ^{1}H NMR δ 0.8 (br t, 3 H), 1.1–1.4 (m, 8 H), 2.2 (m, 2 H), 3.1 (s, 3 H), 3.4 (d, J = 5 Hz, 2 H), 4.4 (m, 1 H), 6.0 (m, 1 H); MS m/z (rel intensity) 185 (M^+ + H, 18), 169 (9), 113 (37), 85 (33), 71 (22), 43 (100).

General Procedure for the One-Pot Preparation of γ-Keto Aldehydes 4. A mixture of 1-methoxy-2-alkyn-4-ol (2 mmol), $IrH_5[P(Pr\text{-}i)_3]_2$ (0.05 mmol), and i-Pr_3P (0.2 mmol) was refluxed in toluene (5 mL) until TLC showed that the reaction was complete. After cooling the mixture, solvent was removed under reduced pressure. Acetone (4.5 mL), water (0.5 mL), and a drop of concentrated hydrochloric acid were added. The mixture was heated at reflux for 30–45 min, cooled, and diluted with ether (20 mL). The extract was washed to neutrality with a saturated sodium chloride solution, dried over sodium sulfate, and then rotary evaporated. The residue was chromatographed on a column of silica gel, eluting with 20% ethyl acetate in petroleum ether, to give pure γ-keto aldehyde. The spectral data for 4-oxoheptanal (4a), 4-oxooctanal (4b), 4-oxononanal (4c), and 4-oxodecanal (4d) were identical with those in the literature.[7]

1-Methoxy-11-(methoxycarbonyl)-2-undecyn-4-ol (8). Methyl 9-oxononanoate (7) was prepared by esterification[18] of oleic acid with methanol followed by ozonization[19] of the double bond. A solution of methyl propargyl ether (1.5 g, 0.021 mol) in 90 mL of THF was cooled to −78 °C and treated with a 1.35 M solution of n-BuLi (15.9 mL, 0.021 mol) in hexane. After the mixture had been stirred for 30 min at −70 °C, methyl 9-oxononanoate (7), (3.6 g, 0.019 mol) in 20 mL of THF was slowly added. Stirring was continued while the mixture was slowly warmed to 0 °C. Then the mixture was diluted with water (10 mL) and extracted with ether (3 × 20 mL). The organic layers were combined and washed to neutrality with a saturated sodium chloride solution (4 × 60 mL), dried over $MgSO_4$, and concentrated. Chromatography of the residue on a column of silica gel, eluting with 50% ethyl acetate in petroleum ether, gave 8 (4.3 g, 87%) as a colorless oil: IR (neat) 3375, 2200, 1730, 1100 cm^{-1}; ^{1}H NMR δ 1.2–1.8 (m, 12 H), 2.2 (m, 2 H), 3.1 (s, 1 H), 3.3 (s, 3 H), 3.5 (s, 3 H), 4.0 (s, 2 H), 4.2 (m, 1 H); MS m/z (rel intensity) 255 (M^+ – H, 1), 186 (4), 158 (33), 99 (16), 69 (51), 59 (30), 55 (100). Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.66; H, 9.30.

Methyl 9-Oxo-12-dodecanoate (9).[15] According to the general procedure, 8 (530 mg, 2.1 mmol) was treated with $IrH_5[P(Pr\text{-}i)_3]_2$ (53 mg, 0.10 mmol) and i-Pr_3P (83 mg, 0.41 mmol) in toluene (10 mL) followed by hydrolysis to give 9 (270 mg, 54%) as a yellow oil. The spectral data were identical with those reported in the literature.[15]

1-Methoxy-7-oxo-2-decyn-4-ol (11), prepared according to the procedure[20] of Vaskan and Kovalev from the Grignard reagent of methyl propargyl ether (1.7 g, 0.025 mol) and 4-oxoheptanal (4a) (2.5 g, 0.020 mol), was obtained as a colorless oil (3.1 g, 79%): IR (neat) 3375, 1710, 1100 cm^{-1}; ^{1}H NMR δ 0.8 (t, J = 8 Hz, 3 H), 1.5 (m, 4 H), 2.3 (m, 4 H), 3.2 (s, 3 H), 3.7 (m, 1 H), 4.0 (s, 2 H), 4.2 (m, 1 H); MS m/z (rel intensity) 199 (M^+ + H, 3), 198 (M^+, 2), 181 (100), 149 (59). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.66; H, 8.88.

4,7-Dioxodecanal (12), prepared from 11 by the general one-pot procedure, was obtained as a pale yellow oil (190 mg, 58%): IR (neat) 2720, 1720, 1710 cm^{-1}; ^{1}H NMR δ 0.8 (t, J = 7 Hz, 3 H), 1.4 (m, 2 H), 2.3 (t, J = 7 Hz, 2 H), 2.55 (s, 4 H), 2.60 (s, 4 H), 9.7 (s, 1 H); MS m/z (rel intensity) 184 (M^+, 11), 156 (14), 141 (16), 127 (18), 113 (45), 99 (18), 85 (37), 71 (89), 57 (23), 43 (100); HRMS calcd exact mass for $C_{10}H_{16}O_3$ 184.1100, found 184.1098.

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Registry No. 1a, 1817-53-4; **1b**, 136015-83-3; **1c**, 136015-84-4; **1d**, 136015-85-5; **2a**, 136015-86-6; **2b**, 136015-87-7; **2c**, 136015-88-8; **2d**, 120507-11-1; **4a**, 74327-28-9; **4b**, 66662-22-4; **4c**, 74327-29-0; **4d**, 43160-78-7; **7**, 1931-63-1; **8**, 136015-89-9; **9**, 50266-44-9; **11**, 136015-90-2; **12**, 136015-91-3; $IrH_5[P(Pr\text{-}i)_3]_2$, 53470-70-5; C_3H_7CHO, 123-72-8; C_4H_9CHO, 110-62-3; $C_5H_{11}CHO$, 66-25-1; $C_6H_{13}CHO$, 111-71-7; methyl propargyl ether, 627-41-8.

Supplementary Material Available: ^{1}H NMR spectra of **1b**, **1c**, **1d**, **2a**, **2b**, **2c**, and **12** (7 pages). Ordering information is given on any current masthead page.

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