New Methods for the Synthesis of 3(2*H*)-Furanones and 2(5*H*)-Furanones

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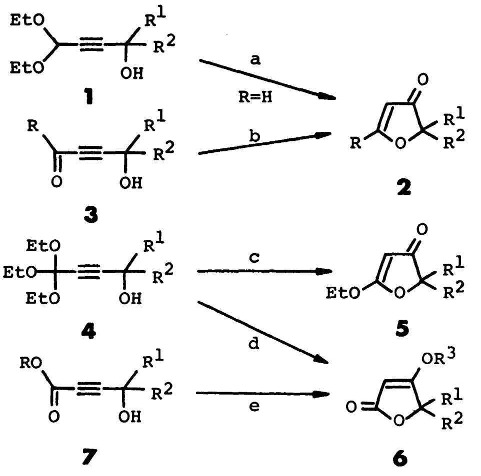
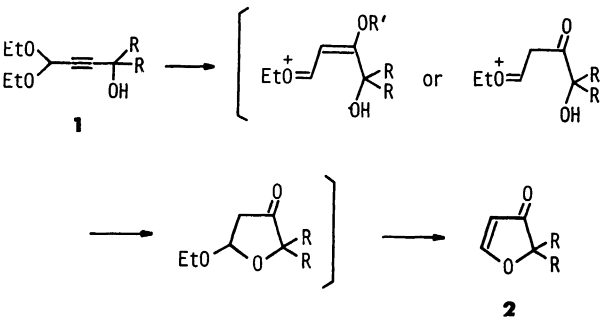
New procedures for the synthesis of 3(2*H*)-furanones and 4-alkoxy-2(5*H*)-furanones are reported. Reaction of ketones with the lithium salt of propynal diethyl acetal, followed by treatment of the resulting 4-hydroxy-2-alkynal diethyl acetals with sulfuric acid–methanol, gave 2,2-disubstituted 3(2*H*)-furanones. The action of a polymer reagent Hg/Nafion-H upon 4–hydroxy-2-alkynones produced 2,2,5-trisubstituted 3(2*H*)-furanones. Reaction of 1,1,1-triethoxy-2-alkyn-4-ols (**4**) with trifluoroacetic acid and mercury(II) acetate provided 5-ethoxy-2,2-disubstituted 3(2*H*)-furanones. In contrast, the adducts **4** were converted into 4-alkoxy-5,5-disubstituted 2(5*H*)-furanones upon reaction with Hg/Nafion-H.

In the preceding paper we have reported new methods for regiocontrolled synthesis of 4,5-dihydro-3(2*H*)-furanones from 2-butyne-1,4-diol derivatives.[1] As the final step of the procedure was the oxidation to 3(2*H*)-furanones, it was anticipated that employing the derivatives of 2-butyne-1,4-diols with higher oxidation stage as the starting materials would lead to 3(2*H*)-furanones[2] directly. This was indeed the case as demonstrated by the reactions summarized in Scheme 1.



a) H_2SO_4–MeOH; b,d,e) Hg/Nafion-H;
c) CF_3COOH, $Hg(OAc)_2$.
Scheme 1.

Transformation of 4-Hydroxy-2-alkynal Diethyl Acetals ***1*** *into 3(2*H*)-Furanones* ***2***. The carbonyl addition of the lithiated propynal diethyl acetals to ketones produced the acetylenic alcohols **1**.[3] Treatment of the adducts **1** with a 1 : 1 mixture of sulfuric acid and methanol at 0 °C gave 3(2*H*)-furanones **2**.[4] Results are summarized in Table 1. The new transformation is understood in terms of the sequence in Scheme 2. Initial elimination of an ethoxyl group and hydration of the triple bond are followed by intramolecular nucleophilic attack of the tertiary hydroxyl group. The Baldwin's rule[5] says that the 5-*exo-trig.* reaction is allowed. It is worthy to note that the propargylic tertiary hydroxyl group in **1** remains intact under the acidic conditions.[6]



Scheme 2.

*Synthesis of 3(2*H*)-Furanones* ***2*** *from 4-Hydroxy-2-alkynones* ***3***. The hydroxy ketones **3** were previously prepared by MnO_2 oxidation of the corresponding 2-butyne-1,4-diols in poor yields.[7,8] We found that treatment of the 2-butyne-1,4-diol derivatives with *t*-butyl hydroperoxide and Nafion-H[9] at 25 °C provided ketones **3** effectively. They were converted by step b in Scheme 1 into 3(2*H*)-furanones **2** in excellent yields with Hg/Nafion-H reagent[1] in the presence of 5 equivalents of water in ethanol at 40 °C[10] (Table 2). The conjugate addition of water to the triple bond took place efficiently with complete regioselectivity.

The combined process was applied to the synthesis of a naturally occurring 3(2*H*)-furanone, bullatenone (**2f**)[11] of Table 2. Oxidation of 4-methyl-1-phenyl-2-pentyne-1,4-diol with *t*-butyl hydroperoxide and Nafion-H followed by treatment with Hg/Nafion-H gave the furanone **2f** in a quantitative yield.

Transformation of 1,1,1-Triethoxy-2-alkyn-4-ols ***4*** *into 5-Ethoxy-3(2*H*)-furanones* ***5*** *and 4-Alkoxy-2(5*H*)-furanones* ***6***. The starting alkynols **4** were prepared by the reaction of ketones with the lithium salt of 3,3,3-triethoxypropyne in THF. Treatment of the adduct **4** with trifluoroacetic acid and mercury(II) acetate at reflux temperature (step c in Scheme 1) afforded the 3-furanones **5** in moderate yields (Table 3).

On the other hand, the reaction of the ortho ester **4a** with the Hg/Nafion-H reagent and 5 equivalents of water in ethanol gave 2(5*H*)-furanone[12] **6a** in 81% yield (step d in Scheme 1). This transformation could

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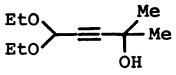
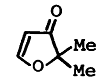
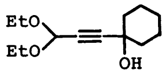
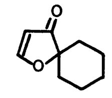
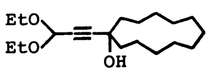
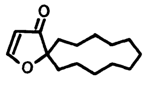
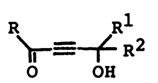
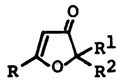
Table 1. 3(2*H*)-Furanones **2** from 4-hydroxy-2-alkynal diethyl acetals **1**

Ketone	Yield/% of the adduct[a,b]		Yield/% of 3(2*H*)-furanone[a,c]	
Acetone	 **1a**	64	 **2a**	98
Cyclohexanone	 **1b**	99	 **2b**	67
Cyclododecanone	 **1c**	79	 **2c**	70

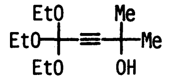
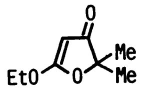
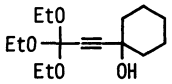
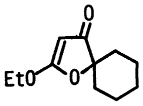
a) Isolated yields. b) Ketones were allowed to react with the lithium salt of propynal diethyl acetal. c) The adducts **1** were treated with H_2SO_4–MeOH.

Table 2. Transformation of 4-hydroxy-2-alkynones **3** into 3(2*H*)-furanones **2**

					Yield/%[a,b]
	R	R^1	R^2		
3a	Me	Me	Me	**2d**	92
3b	Me		$-(CH_2)_5-$	**2e**	87
3c	Ph	Me	Me	**2f**	100
3d		$-(CH_2)_8-$	H	**2g**	90[c]

a) Isolated yields. b) Alkynols **3** were treated with Hg/Nafion-H. c) 4-Acetoxy-2-cyclododecyn-1-one was employed as a starting material.

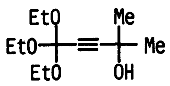
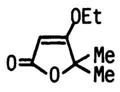
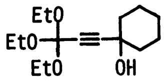
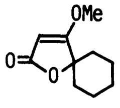
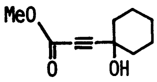
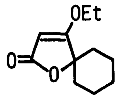
Table 3. Synthesis of 5-ethoxy-3(2*H*)-furanones **5** from 1,1,1-triethoxy-2-alkyn-4-ols **4**

Ketone	Yield/% of the adduct[a,b]		Yield/% of 3(2*H*)-furanone[b,c]	
Acetone	 **4a**	67	 **5a**	63
Cyclohexanone	 **4b**	66	 **5b**	49

a) Ketones were allowed to react with lithium salt of triethyl orthopropiolate. b) Isolated yields. c) The adducts **4** were treated with CF_3CO_2H–$Hg(OAc)_2$.

be effected by a mixture of sulfuric acid–methanol less efficiently[13] (Table 4). Monitoring experiments revealed the intermediacy of ethyl 4-hydroxy-2-alkynoates. Thus the methyl ester **7b** generated independently gave the 2(5*H*)-furanone **6c** on treatment with Hg/Nafion-H (step e in Scheme 1).

Table 4. Synthesis of 4-alkoxy-2(5*H*)-furanones **6**

Starting alkynol	Yield/% of **6**[a]	
 **4a**	 **6a**	81[b]
 **4b**	 **6b**	30[c]
 **7b**	 **6c**	85[b]

a) Isolated yields. b) Hg/Nafion-H was used for the cyclization. c) The alkynol **4b** was treated with H_2SO_4–MeOH.

Experimental

Distillation was carried out by use of Kugelrohr (Büchi) and boiling points were determined by measuring the bath temperature. All mp and bp are not corrected. ^{1}H-NMR spectra (tetramethylsilane as an internal standard) were obtained on a Varian EM 390 spectrometer, chemical shifts being given in ppm units, IR spectra of neat liquid film samples (unless otherwise noted) on a Shimadzu IR-27G spectrometer, MS on a Hitachi RMU-6L spectrometer, and exact mass on a Hitachi M 80 spectrometer. Gas-liquid phase chromatography (GLC) analyses were performed with a Yanagimoto GCG-550F chromatograph, and preparative GLC with a JEOL JGC-20K chromatograph. Preparative TLC plates were prepared with Merck Kiesel-gel PF_{254}. Column chromatography was carried out with silica gel (Wakogel C-100) at atmospheric pressure. Commercial sulfuric acid (97%) and *t*-butyl hydroperoxide (Nakarai Chemicals Ltd., 70% aqueous solution) were used.

*Synthesis of 1-Oxaspiro[4.11]hexadec-2-en-4-one (**2c**) from Cyclo-*

dodecanone (A Typical Procedure). To a THF (10 ml) solution of propynal diethyl acetal[14)] (0.96 g, 7.5 mmol) was added a hexane solution of butyllithium (1.85 M,** 4.1 ml, 7.5 mmol) at −78 °C. After 10 min cyclododecanone (0.91 g, 5.0 mmol) dissolved in THF (7 ml) was added in 15 min. The reaction mixture was stirred at −78 °C for 1 h and at 25 °C for 30 min. Workup followed by column chromatography (hexane–ether 5 : 1) gave 1-(3,3-diethoxypropynyl)cyclododecanol **1c** (1.22 g, 79% yield). Mp 45.0—45.5 °C (hexane); bp 192—193 °C (bath temp)/0.15 Torr;†† ^{1}H-NMR (CCl_4): δ=1.19 (t, J=7.5 Hz, 6H), 1.2—2.2 (m, 23H), 3.3—3.8 (m, 4H), 5.11 (s, 1H); IR: 3430, 2270, 1121, 1055, 1008 cm^{-1}; MS: *m/e* (rel intensity) 310 (M^+, 5), 265(20), 149(8), 119(98), 117(100), 103(60). Found: C, 73.25; H, 11.02%. Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04%.

The adduct **1c** (0.22 g, 0.71 mmol) was dissolved in methanol (1.0 ml) and cooled at 0 °C. To this solution was added sulfuric acid (1.0 ml) dropwise over 10 min. After stirring for 30 min, the reaction mixture was diluted with ether and neutralized with aqueous sodium hydrogencarbonate solution. Extractive workup followed by preparative TLC purification (hexane–ether 1 : 1, R_f 0.33—0.47) gave **2c** (0.12 g, 70% yield). Mp 81.0—81.5 °C (hexane); IR (Nujol): 1709, 1684, 1569 cm^{-1}; ^{1}H-NMR (CCl_4): δ=1.2—1.8 (m, 22H), 5.43 (d, J=2.7 Hz, 1H), 8.04 (d, J=2.7 Hz, 1H); MS: *m/e* (rel intensity) 236 (M^+, 32), 123(32), 110(31), 97(100). Found: C, 75.92; H, 10.23%. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24%.

This procedure applies to the synthesis of **1a**, **1b**, **2a**, and **2b**, whose physical properties are summarized below.

5,5-Diethoxy-2-methyl-3-pentyn-2-ol (1a).[3a)] ^{1}H-NMR (CCl_4): δ=1.19 (t, J=7.5 Hz, 6H), 1.48 (s, 6H), 2.96 (br s, 1H), 3.3—3.8 (m, 4H), 5.12 (s, 1H); IR: 3400, 2270, 1104, 1045, 1009 cm^{-1}; (Found: *m/e* 185.1198, M^+-1).

*5,5-Dimethyl-3(2*H*)-furanone (2a).*[15)] ^{1}H-NMR (CCl_4): δ=1.33 (s, 6H), 5.48 (d, J=2.7 Hz), 8.06 (d, J=2.7 Hz, 1H); IR: 1702, 1555, 794 cm^{-1}; MS: *m/e* 112 (M^+).

1-(3,3-Diethoxypropynyl)cyclohexanol (1b). Bp 103—110 °C (bath temp)/0.05 Torr; ^{1}H-NMR (CCl_4): δ=1.20 (t, J=7.5 Hz, 6H), 1.2—2.0 (m, 10H), 2.6—3.0 (m, 1H), 3.3—3.9 (m, 4H), 5.15 (s, 1H); IR: 3405, 2260, 1112, 1048, 1005 cm^{-1}; MS: *m/e* (rel intensity) 226 (M^+, 5), 197(3), 181(100), 153(29), 107(25), 79(35), 55(57). Found: C, 68.81; H, 9.74%. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80%.

1-Oxaspiro[4.5]dec-2-en-4-one (2b).[16)] ^{1}H-NMR (CCl_4): δ=1.1—2.0 (m, 10H), 5.48 (d, J=2.6 Hz, 1H), 8.09 (d, J=2.6 Hz, 1H); IR: 1700, 1562, 1173 cm^{-1}; MS: *m/e* 152 (M^+).

Transformation of 4-Hydroxy-4-methyl-1-phenyl-2-pentyn-1-one (3c) into Bullatenone (2f) (A Typical Procedure). 4-Methyl-1-phenyl-2-pentyne-1,4-diol[1)] (28 mg, 0.15 mmol) was treated with Nafion®-H[1,9)] (24 mg) in 70% aqueous *t*-butyl hydroperoxide (1 ml) at 25 °C for 42 h. The reaction mixture was filtered, and the catalyst was washed with dichloromethane. Concentration of the combined filtrates *in vacuo* afforded **3c**[10a)] (28 mg) quantitatively. An ethanol (1 ml) solution of **3c** (37 mg, 0.20 mmol) was stirred with Hg/Nafion-H[1)] (52 mg) in the presence of water (18 mg, 1.0 mmol) at 40 °C for 14 h. Removal of the polymer reagent by filtration and concentration of the filtrate gave bullatenone (**2f**)[11)] (37 mg, 100%) whose spectral data were identical with the recorded ones.

Spectral properties of **2d** and **3e** are listed below.

*2,2,5-Trimethyl-3(2*H*)-furanone (2d)*[17)] *from 3a.*[18)] ^{1}H-NMR (CCl_4): δ=1.29 (s, 6H), 2.17 (s, 3H), 5.20 (s, 1H); IR: 1700, 1601, 1390, 1179 cm^{-1}; MS: *m/e* 126 (M^+).

2-Methyl-1-oxaspiro[4.5]dec-2-en-4-one (2e)[19)] *from 3b.*[20)] ^{1}H-NMR (CCl_4): δ=1.0—2.1 (m, 10H), 2.21 (s, 3H), 5.26 (s, 1H); IR: 1697, 1601, 1386, 1348, 1062 cm^{-1}; MS: *m/e* 166 (M^+).

*13-Oxabicyclo[8.2.1]tridec-1(12)-en-11-one-1(**2g**).* 2-Cyclododecyne-1,4-diol[21)] (284 mg, 1.5 mmol) was treated with acetic anhydride (148 mg, 1.5 mmol) and pyridine (1 ml) at 25 °C for 5 h, and the reaction mixture was concentrated. Purification of the residue by column chromatography (hexane–ethyl acetate 5 : 1) gave 4-acetoxy-2-cyclodecynol (159 mg, 46% yield) together with the diol (76 mg) and the diacetate (92 mg). ^{1}H-NMR (CCl_4) of the monoacetate: δ= δ=1.1—2.1 (m+s (δ=2.00), 20H), 4.2—4.4 (m, 1H), 5.1—5.4 (m, 1H); IR: 3430, 1741, 1229, 1020 cm^{-1}; MS: *m/e* 238 (M^+).

A dichloromethane (3 ml) solution of the monoacetate (64 mg, 0.27 mmol) was added to pyridinium chlorochromate (87 mg, 0.40 mmol) and sodium acetate (7 mg, 0.08 mmol) in dichloromethane (0.5 ml) at 0 °C. After stirring for 6 h at 25 °C, workup followed by column chromatography (ether) gave 4-acetoxy-2-cyclododecyn-1-one (55 mg, 90% yield). Bp 140—142 °C (bath temp)/0.09 Torr; ^{1}H-NMR (CCl_4): δ=1.1—2.1 (m+s (δ=2.04), 17H), 2.3—2.6 (m, 2H), 5.46 (t, J=6.0 Hz, 1H); IR: 2250, 1742, 1672, 1218, 1020 cm^{-1}; MS: *m/e* (rel intensity) 236 (M^+, trace), 194(3), 123(11), 97(17), 79(17), 55(21), 43(100). Found: C, 70.91; H, 8.51%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

An ethanol (0.5 ml) solution of the acetylenic ketone (30 mg 0.13 mmol) was stirred with Hg/Nafion-H (31 mg) in the presence of water (11 mg, 0.64 mmol) at 40 °C for 7 h. Filtration of the reaction mixture and concentration of the filtrate gave **2g** (22 mg, 90% yield). Mp 60.5—61.5 °C (hexane); ^{1}H-NMR (CCl_4): δ=0.8—2.9 (m, 16H), 4.34 (t, J=7.8 Hz, 1H), 5.34 (s, 1H), IR (CCl_4): 1700, 1590, 1376, 1158 cm^{-1}; MS: *m/e* (rel intensity) 194 (M^+, 5), 148(41), 122(44), 81(55), 69(68), 67(62), 55(74), 40(100). Found: *m/e* 195.1295. Calcd for $C_{12}H_{19}O_2$: M^++1, 195.1383.

Synthesis of 2-Ethoxy-1-oxaspiro[4.5]dec-2-en-4-one (5b) (A Typical Procedure). A hexane solution of butyllithium (1.60 M, 4.4 ml, 7.0 mmol) was added at −78 °C to 3,3,3-triethoxypropyne[22)] (1.20 g, 7.0 mmol) in THF (10 ml). After stirring for 40 min, cyclohexanone (0.97 g, 9.9 mmol) dissolved in THF (6 ml) was added in 20 min. Stirring at −78 °C for 50 min, at 25 °C for 20 min, followed by workup and column chromatography (hexane–ethyl acetate 5 : 1) gave the adduct **4b** (1.24 g, 66% yield). Bp 148—150 °C (bath temp)/0.12 Torr; ^{1}H-NMR (CCl_4): δ=1.0—2.4 (m+t (δ=1.20, J=6.6 Hz), 20H), 3.57 (q, J=6.6 Hz, 6H); IR: 3400, 2230, 1240, 1084, 1041 cm^{-1}; MS: *m/e* (rel intensity) 225 ($M^+-C_2H_5O$, 100), 179(40), 141(26), 105(35), 95(30), 81(30). Found: *m/e* 255.1557. Calcd for $C_{14}H_{23}O_4$: M^+-CH_3, 255.1594.

Trifluoroacetic acid (3 ml) was added at 25 °C to the adduct **4b** (122 mg, 0.45 mmol) and mercury(II) acetate (144 mg, 0.45 mmol). After stirring for 15 min at reflux temperature, workup and preparative TLC purification (hexane–ethyl acetate 2 : 1, double development) gave **5b** (R_f 0.30—0.40, 43 mg, 49% yield). Mp 54.1 °C (hexane); ^{1}H-NMR (CCl_4): δ=1.0—2.0 (m+t (δ=1.48, J=7.5 Hz), 13H), 4.21 (q, J=7.5 Hz, 2H), 4.57 (s, 1H); IR: 1696, 1573, 1427, 1360, 881 cm^{-1}; MS: *m/e* (rel intensity) 197 (M^++1, 4), 196 (M^+, 24), 141(21), 115(21), 83(36), 81(36), 69(77), 40(100). Found: C, 67.44; H, 8.36%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%.

This procedure was applied to the synthesis of **4a** and **5a**.

*4,4,4-Triethoxy-2-methyl-3-pentyn-2-ol (4a) and 2,2-Dimethyl-5-ethoxy-3(2*H*)-furanone (5a).* The ortho ester **4a** showed bp 135—136 °C (bath temp)/0.12 Torr; ^{1}H-NMR (CCl_4):

** 1 M=1 mol dm^{-3}; †† 1 Torr=133.322 Pa.

$\delta=0.80$ (t, $J=7.2$ Hz, 9H), 1.12 (s, 6H), 1.4—1.8 (m, 1H), 3.17 (q, $J=7.2$ Hz, 6H); IR: 3450, 2250, 1240, 1170, 1085, 1034 cm^{-1}; MS: *m/e* (rel intensity) 185 ($M^+-C_2H_5O$, 84), 111(44), 95(100), 71(36), 67(37), 59(42), 43(80). Found: *m/e* 231.1578. Calcd for $C_{12}H_{23}O_4$: M^++1, 231.1594.

Physical properties of the 3-furanone **5a** are given. Bp 98—100 °C (bath temp)/0.13 Torr; ^{1}H-NMR (CCl_4): $\delta=1.39$ (s, 6H), 1.47 (t, $J=7.2$ Hz, 3H), 4.28 (q, $J=7.2$ Hz, 2H), 4.55 (s, 1H); IR: 1675, 1567, 1175, 1057 cm^{-1}; MS: *m/e* (rel intensity) 157 (M^++1, 4), 156 (M^+, 23), 111(2), 97(12), 87(12), 69(100), 59(55), 43(30). Found: *m/e* 156.0885. Calcd for $C_8H_{12}O_3$: M^+, 156.0786.

5,5-Dimethyl-4-ethoxy-2(5H)-furanone (6a). An ethanol (1 ml) solution of **4a** (40 mg, 0.17 mmol) was stirred with Hg/Nafion-H (46 mg) in the presence of water (13 mg, 0.74 mmol) at 40 °C for 40 h. Filtration of the reaction mixture followed by concentration of the filtrate gave **6a**[13a] (22 mg, 81% yield). Bp 114—115 °C (bath temp)/0.12 Torr; ^{1}H-NMR (CCl_4): $\delta=1.41$ (t, $J=6.9$ Hz, 3H), 1.42 (s, 6H), 4.05 (q, $J=6.9$ Hz, 2H), 4.81 (s, 1H); IR: 1754, 1634, 1342, 1266, 1260 cm^{-1}; MS: *m/e* 156 (M^+).

When the reaction was carried out at 25 °C for 1.5 h, ethyl 4-hydroxy-4-methyl-2-pentynoate (**7a**)[23] was produced in a quantitative yield. Bp 100—101 °C (bath temp)/0.5 Torr; ^{1}H-NMR (CCl_4): $\delta=1.29$ (t, $J=7.2$ Hz, 3H), 1.52 (s, 6H), 3.26 (s, 1H), 4.14 (q, $J=7.2$ Hz, 2H); IR: 3410, 2230, 1712, 1253, 1030 cm^{-1}; MS: *m/e* 141 (M^+).

4-Methoxy-1-oxaspiro[4.5]dec-3-en-one (6b). A mixture of sulfuric acid (0.15 ml) and methanol (0.15 ml) was added to **4b** (62 mg, 0.23 mmol) dissolved in methanol (0.15 ml) at 25 °C in 10 min. After stirring for 2 h, workup followed by preparative TLC separation (hexane-ether 1 : 1) gave **6b**[13a] (R_f 0.08—0.12, 13 mg, 30% yield) having ^{1}H-NMR (CCl_4): $\delta=1.0$—2.5 (m, 10H), 3.77 (s, 3H), 5.03 (s, 1H); IR: 1711, 1614, 1228, 1030 cm^{-1}; MS: *m/e* 182 (M^+).

4-Ethoxy-1-oxaspiro[4.5]dec-3-en-2-one (6c). Methyl 4-(1-hydroxycyclohexyl)-2-butynoate (**7b**)[13a] (50 mg, 0.28 mmol) dissolved in ethanol (1 ml) was treated with Hg/Nafion-H (103 mg) in the presence of water (25 mg, 1.4 mmol) at 40 °C for 50 h. Removal of the polymer reagent by filtration and concentration of the filtrate gave **6c** (46 mg, 85% yield). Mp 70—71 °C (hexane); bp 95—97 °C (bath temp)/0.07 Torr; ^{1}H-NMR (CCl_4): $\delta=0.9$—2.1 (m+t($\delta=1.40$, $J=6.8$ Hz), 13H), 4.00 (q, $J=6.8$ Hz, 2H), 4.74 (s, 1H); IR: 1751, 1627, 1336, 1195, 976 cm^{-1}; MS: *m/e* (rel intensity) 196 (M^+, 25), 168(22), 153(28), 140(56), 125(34), 112(41), 69(100), 55(56), 43(31). Found: C, 67.37; H, 8.48%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%.

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