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Oxidative Substitution Reactions of Organostannyl Compounds with Lead Tetraacetate. A Convenient Route to 5-Alkylidene-2(5*H*)-furanones

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5-Substituted 2-tributylstannylfurans which were synthesized by the reaction of corresponding 5-substituted 2-lithiofurans with tributylstannyl chloride, were treated with two equimolar amounts of lead tetraacetate at room temperature to give corresponding 5-substituted 5-acetoxy-2(5*H*)-furanones in good yields. The 5-acetoxy-2(5*H*)-furanone was heated at 80 °C in acetic acid–acetic anhydride containing a catalytic amount of concentrated sulfuric acid to give 5-alkylidene-2(5*H*)-furanone in moderate yield.

Oxidations of an organostannyl group were carried out by treating the tin compounds with chromium(IV) oxide–pyridine complex,[1)] *m*-chloroperbenzoic acid,[2)] lead tetraacetate(LTA)[3)] and others.[4)] Recently we reported that an organostannyl group was oxidatively substituted by an oxygen-functionalized group[5)] or cyclized intramolecularly[6)] by treating an organostannyl compound with LTA.

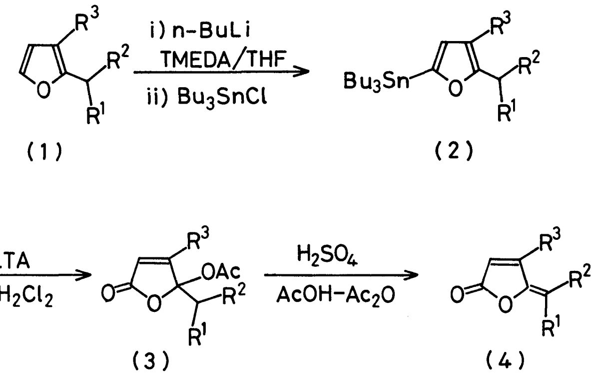
Although the oxidation of a furan ring with LTA has been known to give a 2-acetoxyfuran and/or a 2,5-diacetoxy-2,5-dihydrofuran,[7)] the reaction is not selective and low yield. Also it is known that the oxidation of a 2-siloxyfuran gave a 5-acetoxy-2(5*H*)-furanone.[8)]

We have accomplished a novel and a concurrent oxidation of C–Sn bond at C-2 position and an introduction of an acetoxyl group at C-5 position in the furan ring chemoselectively when various 5-substituted 2-tributylstannylfurans were treated with LTA.[9)] By joining this oxidative substitution and a known acetic acid elimination method,[10)] we could find a convenient route to the synthesis of 5-alkylidene-2(5*H*)-furanones. This paper will describe the LTA oxidation of a 2-stannylfuran to a 5-acetoxy-2(5*H*)-furanone and the synthesis of 5-alkylidene-2(5*H*)-furanone in detail.

2-Tributylstannylfurans (**2**) were synthesized in excellent yields by the reaction of corresponding 5-substituted furans (**1**) with butyllithium under the existence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and tributylstannyl chloride in tetrahydrofuran (THF) at −78 °C. Stannylated furans (**2**) are unstable, so it is necessary to use immediately for the next reaction. 2-Methyl-5-tributylstannylfuran (**2a**) was treated with an equimolar amount of LTA in dichloromethane at room temperature for 3 d to give 5-acetoxy-5-methyl-2(5*H*)-furanone (**3a**) in 91% yield (based on LTA) accompanied with quantitative yield of stannyl acetate (Scheme 1).

The fact that the concurrent oxidation of two positions in the furan ring of **2a** suggested that two molar equivalents of LTA is necessary for this oxidation reaction. This was supported by the following results that the oxidation of **2d** gave only 15% of **3d** when an equimolar amount of LTA was used. However, two molar equivalents of LTA was used, **2d** was converted to **3d** in 67% yield.

The substrates (**2f**) and (**2g**) which bear an ether group gave the desired 5-acetoxy-2(5*H*)-furanones (**3f**)(30%) and (**3g**)(21%), respectively. In the case of **2f** considerable amount of a destannylated product (**1f**)(55%)

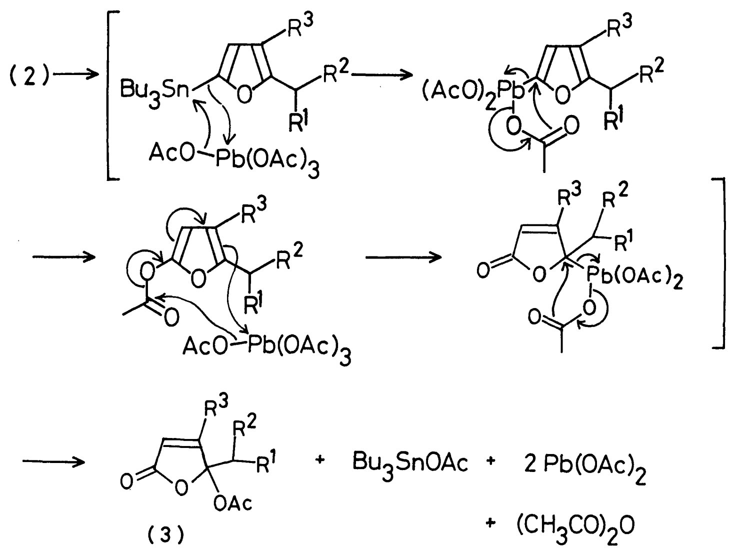


Scheme 1.

Table 1. Yields of Stannylated Compound (**2**), Acetoxyfuranone (**3**), and 5-Alkylidene-2(5*H*)-furanone (**4**)

Entry	R¹	R²	R³	Yield (%)^a)		
				2	**3**	**4**
a	H	H	H	99	91	(53%)^d)
b	Pr	H	H	91	96	95
c	PhCH$_2$	H	H	72	55	43
d	Me	H	Ph	98	67^b)	75
e	H	H	CH$_2$OMe	77	52	51^e)
f	OCH$_2$OMe	H	H	99	30^c)	0
g	OMe	H	H	99	21	0
h	Me	Me	Ph	90	53	82
i	CHMe$_2$	H	Ph	98	43	—^f)

a) Yields based on LTA. b) Yield based on **2d**. c) Destannylated product **1f** (55%) was also obtained. d) Instead of the desired **4a**, Anemonin (**5**) was obtained. e) Diacetate (**6**) (15%) was also yielded. f) Elimination of acetic acid did not carry out.



Scheme 2.

was obtained (Table 1).

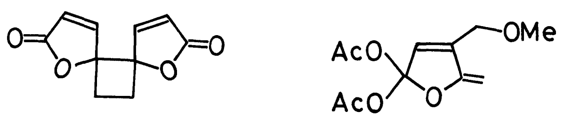
From these observations a plausible reaction mechanism was proposed in Scheme 2.

A 5-acetoxy-2(5*H*)-furanone **3** was heated at 80 °C in acetic acid–acetic anhydride containing a catalytic amount of concentrated sulfuric acid[10] to give a 5-alkylidene-2(5*H*)-furanone **4** as a sole product (Scheme 1 and 3). However, the compound **3a** gave the natural product, Anemonin (**5**),[10,11] which was the dimerized product of protoanemonin (**4a**).

In the reaction of **3e** the desired 5-alkylidene-2(5*H*)-furanone (**4e**) was obtained in 51% yield, and in addition to this, unstable diacetate (**6**)(15%) was also detected. However, none of the desired product **4f** or **4g** was detected in the reaction of **3f** or **3g**.

We also have applied this alkylidene-2(5*H*)-furanone synthesis to a bicyclic furan (**7**). 4,5,6,7-Tetrahydro-3,6-dimethylbenzofuran (Menthofuran) (**7**) was stannylated at α-position of the furan ring followed by LTA oxidation to give the corresponding acetoxyfuranone **9**. Compound **9** is known as Bursera lactone acetate, which was formed from the oxidation of menthofuran followed by acetoxylation.[12] Elimination of acetic acid molecule gave 5,6-dihydro-3,6-dimethylbenzofuran-2(4*H*)-one (**10**)(81%) (Scheme 4).

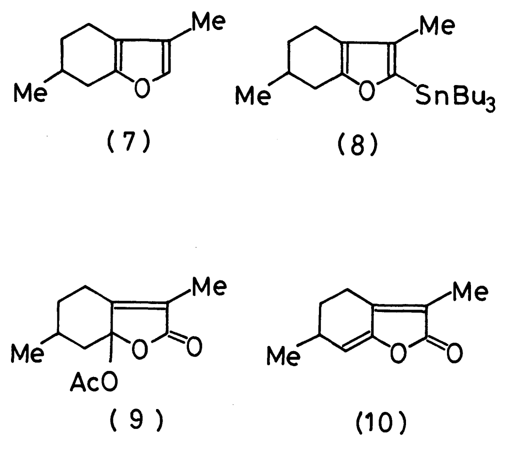
We have thus demonstrated that the combining method of LTA oxidation of 2-stannylfuran derivatives and the elimination of an acetic acid molecule is a useful method for the synthesis of 5-alkylidene-2(5*H*)-furanones.



Anemonin
(5)

(6)

Scheme 3.



(7) (8) (9) (10)

Scheme 4.

Experimental

General Methods: Melting points were measured with a Yanako MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were observed with Hitachi R-24B, R-600 and JEOL JNM-GSX 400 spectrometers. ^{13}C NMR spectra were recorded on JEOL JNM-FX 270, JNM-GSX 400 and JNM-GSX 500 spectrometers. Chemical shifts were described in parts per million (δ) relative to tetramethylsilane (TMS) as an internal standard in CCl_4 or $CDCl_3$. Infrared spectra were obtained on a JASCO A-202 infrared spectrometer. Mass spectra were taken with Hitachi RMU-60 and RMR-7M mass spectrometers at 70 eV. Column chromatography was performed on Merck Art 7734, Fujigel BW-820MH and BW-200. Thin-layer chromatography was performed on Merck Art 7731. Unless otherwise noted, materials were obtained from commercial suppliers. Dichloromethane was distilled from calcium hydride. THF was distilled from lithium aluminum hydride and stored over molecular sieves 5A 1/16. Unless otherwise noted, other solvents were used after simple distillation.

Stannylation of Furans: General Procedure A: To a stirred solution of furan **1** (5 mmol) and TMEDA (1.7 ml) in dry THF (5 ml) was added dropwise a hexane solution of butyllithium (3.3 ml, 5.0 mmol)(1.5 M solution 1M=1 mol dm^{-3}) at −78 °C, and the reaction mixture was stirred for 2 h at −40 °C—−20 °C. The mixture was again cooled to −78 °C, and a solution of tributylstannyl chloride (1.63 g, 5.0 mmol) in dry THF (2.5 ml) was added dropwise. After 30 min the mixture was allowed to warm to room temperature and stirred overnight. The resulting reaction mixture was quenched with cold water and extracted with ether. The combined extracts were washed with saturated sodium hydrogencarbonate solution, brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was passed through a short alumina plug with hexane. Removal of the solvent gave pure 2-tributylstannylfuran **2** as colorless liquid. Stannylfuran **2** is quite unstable, so it must be used immediately for the next reaction.

2-Methyl-5-tributylstannylfuran (2a): ^{1}H NMR (CCl_4) δ= 0.75—1.65 (m, 27H), 2.32(d, 3H, J=1.8 Hz), 5.85(dd, 1H, J=3.0 and 1.8 Hz), and 6.30(d, 1H, J=3.0 Hz).

2-Butyl-5-tributylstannylfuran (2b): IR (neat) 2960, 2875, 1590, 1460, 1375, and 1005 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.75—1.65(m, 34H), 2.66(t, 2H, J=6.6 Hz), 5.88(d, 1H, J=3.0 Hz), and 6.33(d, 1H, J=3.0 Hz).

2-Phenethyl-5-tributylstannylfuran (2c): ^{1}H NMR (CCl_4) δ=0.75—1.85 (m, 27H), 2.95(s, 4H), 5.85(d, 1H, J=3.0 Hz), 6.35(d, 1H, J=3.0 Hz), and 7.15(s, 5H).

2-Ethyl-3-phenyl-5-tributylstannylfuran (2d): IR (neat) 2970, 2875, 1610, 1455, 1375, 1195, and 1030 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.75—1.65(m, 30H), 2.81(q, 2H, J=7.5 Hz), 6.54(s, 1H), and 7.26(m, 5H).

3-Methoxymethyl-2-methyl-5-tributylstannylfuran (2e): ^{1}H NMR (CCl_4) δ=0.75—1.65(m, 27H), 2.27(s, 3H), 3.20(s, 3H), 4.15(s, 2H), and 6.36(s, 1H).

2-[(Methoxy)methoxy]methyl-5-tributylstannylfuran (2f): IR (neat) 2965, 2880, 1460, 1375, and 1045 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.75—1.65(m, 27H), 3.31(s, 3H), 4.48(s, 2H), 4.55(s, 2H), 6.23(d, 1H, J=3.0 Hz), and 6.41(d, 1H, J=3.0 Hz).

2-(Methoxy)methyl-5-tributylstannylfuran (2g): ^{1}H NMR (CCl_4) δ=0.70—1.70(m, 27H), 3.24(s, 3H), 4.32(s, 2H), 6.18(d, 1H, J=3.0 Hz), and 6.40(d, 1H, J=3.0 Hz).

2-Isopropyl-3-phenyl-5-tributylstannylfuran (2h): IR (neat) 2960, 2870, 1610, 1460, 1375, 1060, and 700 cm^{-1}. ^{1}H NMR (CCl_4) 0.75—1.70(m, 33H), 3.13—3.35(m, 1H), 6.53(s, 1H), and 7.26(s, 5H).

2-Isobutyl-3-phenyl-5-tributylstannylfuran (2i): IR (neat) 2960, 2870, 1610, 1460, 1375, 1070, and 700 cm^{-1}. ^{1}H NMR (CCl_4) 0.75—1.70(m, 34H), 2.66(d, 2H, J=7.5 Hz), 6.54(s, 1H), and 7.27(s, 5H).

Oxidation of 2-Tributylstannylfurans (2a)—(2i) with LTA: General Procedure B: The mixture of 2-tributylstannylfuran (5.0 mmol) and LTA (5.0 mmol) in dichloromethane (25 ml) was stirred for 3d at room temperature. After removal of the solvent, the residue was dissolved in ether and the insoluble material was removed by filtration, and the filtrate was treated with saturated aqueous potassium fluoride solution (5 ml). The resulting suspension was filtered, and the filtrate was extracted with ether, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was separated by silica-gel column chromatography with benzene–ethyl acetate to give pure 5-acetoxy-2(5*H*)-furanone (**3**).

5-Acetoxy-5-methyl-2(5*H*)-furanone (3a): According to the general procedure B, from 8.68 g (23.4 mmol) of **2a** and 11.4 g (90% assay, 23.2 mmol) of LTA, **3a** was obtained in 91% yield (1.65 g, based on LTA). IR(neat) 3130, 2960, 1790, and 1760 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.82(s, 3H), 2.05(s, 3H), 6.10(d, 1H, J=6.0 Hz), and 7.64(d, 1H, J=6.0 Hz). High Res. MS(m/z); Found: M^+ −42, 114.0307, Calcd for $C_5H_6O_3$: M−42, 114.0316.

5-Acetoxy-5-butyl-2(5*H*)-furanone (3b): From 1.73 g (4.20 mmol) of **2b** and 2.17 g (4.40 mmol) of LTA, 421 mg (96%) of **3b** was yielded. IR(neat) 2960, 2870, 1785, 1775, 1610, 1210, 1070, and 1010 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.75—1.05(m, 3H), 1.15—1.50(m, 4H), 1.99(s, 3H), 1.90—2.15(m, 2H), 6.09(d, 1H, J=3.0 Hz), and 7.54(d, 1H, J=3.0 Hz). Found: C, 60.88; H, 7.01%. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12%.

5-Acetoxy-5-phenethyl-2(5*H*)-furanone (3c): From 2.06 g (4.5 mmol) of **2c** and 2.31 g (4.7 mmol) of LTA, compound **3c** was obtained in 55% yield (317 mg). IR(neat) 3030, 2950, 1780, 1750, 1600, 1225, 1065, and 1020 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.96(s, 3H), 2.3—2.7(m, 4H), 6.11(d, 1H, J=6.0 Hz), 7.18(s, 5H), and 7.56(d, 1H, J=6.0 Hz). Found: C, 68.45; H, 5.60%. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73%.

5-Acetoxy-5-ethyl-4-phenyl-2(5*H*)-furanone (3d): From 2.24 g (4.85 mmol) of **2d** and 4.50 g (9.70 mmol) of LTA, compound **3d** was obtained in 67% (796 mg) yield. IR(neat) 1775, 1610, 1445, 1365, 1210, 1085, and 1045 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.80(t, 3H, J=7.5 Hz), 2.01(s, 3H), 2.34(q, 2H, J=7.5 Hz), 6.42(s, 1H), and 7.52(m, 5H). ^{13}C NMR ($CDCl_3$) δ=6.61(q), 20.35(q), 30.55(t), 107.9(s), 116.6(d), 127.3(s×2), 128.0(d), 129.3(d×2), 131.6(d), 162.5(s), 168.0(s), and 169.2(s). High Res. MS(m/z) Found: M^+−CH_2CO, 204.2258, Calcd for $C_{12}H_{12}O_3$: M−CH_2CO, 204.2268.

According to the general procedure B, 1.38 g (3.0 mmol) of **2d** was treated with 1.44 g (3.1 mmol) of LTA to give 111 mg (15.1%) of **3d**, and 610 mg(44.1%) of starting material **2d** was recovered.

5-Acetoxy-4-(methoxymethyl)-5-methyl-2(5*H*)-furanone (3e): From 1.74 g (4.19 mmol) of **2e** and 4.34 g (90% assay, 8.81 mmol) of LTA, 430 mg(52%) of **3e** was obtained. Compound **3e** is unstable. IR (neat) 1780, 1765, 1660, 1370, 1210, 1060, and 1010 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.70(s, 3H), 2.01(s, 3H), 3.39(s, 3H), 4.20(d, 2H, J=1.2 Hz), and 5.99(d, 1H, J=1.2 Hz).

5-Acetoxy-5-(methoxy)methoxymethyl-2(5*H*)-furanone (3f): From 2.07 g (4.81 mmol) of **2f** and 4.47 g (9.62 mmol) of LTA, 317 mg (30%) of **3f** and 377 mg (55%) of **1f** were yielded. Compound **3f** is also unstable. IR (neat) of **3f** 2960, 1780, 1760, 1610, 1210, and 1045 cm^{-1}. ^{1}H NMR (CCl_4) of **3f** δ=2.06(s, 3H), 3.30(s, 3H), 3.83(d, 1H, J=11.0 Hz), 3.91(d, 1H, J=11.0 Hz), 4.60(s, 2H), 6.21(d, 1H, J=5.4 Hz), and 7.54(d, 1H, J=5.4 Hz).

5-Acetoxy-5-methoxymethyl-2(5*H*)-furanone (3g): From 2.48 g (6.2 mmol) of **2g** and 6.40 g (90% assay, 13.0 mmol) of LTA, 236 mg (21%) of **3g** was obtained. Compound **3g** is also unstable. IR (neat) 1780, 1760, 1610, 1370, 1210, 1115, 1080, and 1040 cm^{-1}. ^{1}H NMR (CCl_4) δ=2.07(s, 3H), 3.39(s, 3H), 3.60(d, 1H, J=10.5 Hz), 3.89(d, 1H, J=10.5 Hz), 6.16(d, 1H, J=6.0 Hz) and 7.51(d, 1H, J=6.0 Hz). ^{13}C NMR ($CDCl_3$) δ=21.40(q), 60.06(q), 73.17(t), 106.0(s), 123.9(d), 151.6(d), 168.4(s) and 169.1(s).

5-Acetoxy-5-isopropyl-4-phenyl-2(5*H*)-furanone (3h): From 1.81 g (3.81 mmol) of **2h** and 3.54 g (7.62 mmol) of LTA, **3h** was prepared in 53% (523 mg) yield, mp 96—97 °C (crystallized from benzene–hexane=2 : 1). IR(KBr) 1780, 1760, 1620, 1495, 1370, 1220, 1160, and 990 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.68(d, 3H), 1.28(d, 3H), 2.10(s, 3H), 2.10—2.67(m, 1H), 6.49(s, 1H), and 7.55(m, 5H). ^{13}C NMR ($CDCl_3$) δ=15.42(q), 15.88(q), 21.70(q), 34.61(d), 109.3(s), 116.9(d), 127.3(s), 127.6(s), 128.3(d), 129.2(d), 129.3(d), 131.5(d), 162.5(s), 168.1(s) and 169.6(s). Found: C, 69.26; H, 6.25%. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20%.

5-Acetoxy-5-isobutyl-4-phenyl-2(5*H*)-furanone (3i): From 1.84 g (3.76 mmol) of **2i** and 3.49 g (7.52 mmol) of LTA, **3i** was obtained in 43% (441 mg) yield. IR (neat) 1780, 1760, 1610, 1375, 1230, and 1070 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.84(d, 3H, J=6.5 Hz), 1.00(d, 3H, J=6.5 Hz), 1.79(dd, 1H, J=14.2 and 5.2 Hz), 1.89(m, 1H), 2.08(s, 3H), 2.24(dd, 1H, J=14.2 and 6.5 Hz), 6.49(s, 1H), 7.48(m, 3H), and 7.65(m, 2H). ^{13}C NMR δ=21.43(q), 23.15(q), 23.46(q), 23.70(d), 45.64(t), 107.25(s), 115.83(d), 127.15(d×2), 128.59(s), 129.08(d×2), 131.28(d), 163.11(s), 167.68(s), and 168.96(s). Found: C, 69.88; H, 6.62%. Calcd for $C_{16}H_{18}O_4$; C, 70.05; H, 6.61%.

Synthesis of 5-Alkylidene-2(5*H*)-furanones: General Procedure C: The mixture of 5-acetoxy-2(5*H*)-furanone (3) (2 mmol) in 2 ml of acetic acid, 2 ml of acetic anhydride and 2 drops of concentrated sulfuric acid was heated at 80 °C for 1—2 h. After cooling the resulting mixture was carefully neutralized with saturated sodium hydrogencarbonate solution and the aqueous solution was extracted with ether. The ether layer was washed with brine, dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by silica-gel column chromatography with benzene–ethyl acetate to give pure 5-alkylidene-2(5*H*)-furanone.

Anemonin (5): According to the general procedure C, from 530 mg (3.4 mmol) of **3a** Anemonin (**5**) was obtained in 53% (173 mg) yield, mp 157—158 °C (crystallized from ethanol) (lit,[11] mp 158 °C). IR ($CHCl_3$) 3030, 1775, 1600, 1210, and 1130 cm^{-1}. ^{1}H NMR ($CDCl_3$) 2.35—2.65(m, 4H), 6.15(d, 2H, J=6.0 Hz), 7.78(d, 2H, J=6.0 Hz).

^{13}C NMR ($CDCl_3$) δ=23.93(t×2), 90.38(s×2), 121.11(d×2), 153.36(d×2) and 170.89(s×2). Found: m/z 192.0414. Calcd for $C_{10}H_8O_4$: M, 192.0422.

5-Butylidene-2(5*H*)-furanone (4b): From 535 mg (2.7 mmol) of **3b**, compound **4b** was obtained in 95% (354 mg) as *E*/*Z* mixture (*E*/*Z*=1/3, by ^{1}H NMR). The structure was identified by the NMR spectra with those of the authentic sample.[13] IR (neat) 2975, 2885, 1785, 1755, 1675, 1210, 1070, and 1010 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.97(t, 3H, J=6.6 Hz), 1.53(m, 2H, J=6.6 Hz), 2.36(dt, 2H, J=7.8 and 6.6 Hz), 5.28(bt, 0.75H, *Z*-isomer), 5.71(bt, 0.25H, *E*-isomer), 6.10(d, 0.75H, J=5.4 Hz, (*Z*)), 6.21(bd, 0.25H, J=5.6 Hz, (*E*)), 7.40(d, 0.75H, J=5.4 Hz, (*Z*)), and 7.78(d, 0.25H, J=5.6 Hz, (*E*)). MS(m/z) M^{+}, 138, 82, and 55.

5-Phenethylidene-2(5*H*)-furanone (4c): From 787 mg (3.2 mmol) of **3c**, **4c** was yielded in 43% (256 mg). IR (neat) 3050, 1780, 1760, 1605, and 1070 cm^{-1}. ^{1}H NMR (CCl_4) δ=3.67(d, 2H, J=7.8 Hz), 5.35(t, 1H, J=7.8 Hz), 6.11(d, 1H, J=6.0 Hz), 7.20(s, 5H), and 7.31(d, 1H, J=6.0 Hz). Found: m/z 186.0674. Calcd for $C_{12}H_{10}O_2$: M, 186.0680.

5-Ethylidene-4-phenyl-2(5*H*)-furanone (4d): From 1.01 g (4.1 mmol) of **3d**, compound **4d** was obtained in 75% (572 mg) yield, mp 102—103 °C (crystallized from hexane–benzene =10 : 1). IR (neat) 1765, 1755, 1665, 1440, 1210, 1075, and 1000 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.97(d, 3H, J=7.2 Hz), 5.42(q, 1H, J=7.2 Hz), 6.05(s, 1H), and 7.43(s, 5H). ^{13}C NMR ($CDCl_3$) δ=12.26(q), 112.21(d), 114.98(d), 126.8(s), 128.38(d×2), 129.00(d×2), 130.39(d), 149.82(s), 156.93(s), and 168.85(s). Found: C, 77.40; H, 5.56%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

4-Methoxymethyl-5-methylene-2(5*H*)-furanone (4e): According to the general procedure C, 151 mg (0.75 mmol) of **3e** gave 54 mg (51%) of **4e** and 27 mg (15%) of 2,2-diacetoxy-4-methoxymethyl-5-methylene-2,5-dihydrofuran (**6**). Both compounds **4e** and **6** were quite unstable. ^{1}H NMR (CCl_4) of **4e** δ=3.42(s, 3H), 4.38(d, 2H, J=1.8 Hz), 4.88(dd, 1H, J=2.4 Hz and 0.6 Hz), 5.10(dd, 1H, J=2.4 and 1.8 Hz), and 6.14(d, 1H, J=6.0 Hz). ^{1}H NMR (CCl_4) of **6** δ=2.07(s, 6H), 3.39(s, 3H), 4.21(s, 2H), 4.88(d, 1H, J=2.4 Hz), 5.10(d, 1H, J=2.4 Hz), and 5.64(s, 1H).

Treatment of 3f with Acid: According to the general procedure C, 83 mg (0.38 mmol) of **3f** was treated with acid. But none of the desired 2(5*H*)-furanone was detected.

Treatment of 3g with Acid: According to the general procedure C, 3 g was treated as described above. The reaction was dirty and none of the desired product (**4g**) was detected.

5-Isopropylidene-4-phenyl-2(5*H*)-furanone (4h): From 520 mg (2 mmol) of **3h**, compound **4h** was obtained in 82% (328 mg) yield, mp 130.5—131 °C (crystallized from benzene–hexane=1 : 1). IR ($CHCl_3$) 1760, 1740, 1660, 1580, 1490, 1375, 1260, 1190, 1095, and 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.58(s, 3H), 2.07(s, 3H), 6.02(s, 1H), and 7.39(m, 5H). ^{13}C NMR ($CDCl_3$) δ=19.60(q), 20.90(q), 118.2(d), 126.0(s), 127.9(d×2), 128.6(d×2), 129.4(d), 133.3(s), 144.7(s), 157.0(s), and 168.5(s). Found: C, 78.03; H, 6.07%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

Stannylation of Menthofuran (7): According to the general procedure A, **7** (1.50 g, 10 mmol) was stannylated to give 2-tributylstannylmenthofuran (**8**) in 99%(4.49 g) yield. IR (neat) 2960, 2850, 1635, 1455, 1375, and 1180 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.75—2.05(m, 36H), 2.05—2.70(m, 4H).

7a-Acetoxy-5,6,7,7a-tetrahydro-3,6-dimethylbenzofuran-2(4*H*)-one (9): According to the general procedure B, 2.09 g (4.76 mmol) of stannylated menthofuran (**8**) and 4.42 g (95.5% assay, 9.52 mmol) of LTA gave 763 mg (71%) of **9**. IR (neat) 2790, 2875, 1778, 1698, 1435, 1365, 1217, 1030, and 975 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.99(d, 3H), 1.00—1.19(m, 2H), 1.85(d, 3H, J=1.5 Hz), 1.88(m, 1H), 1.98(m, 1H), 2.05(s, 3H), 2.18(m, 1H), 2.68(dt, 1H, J=13.5 and 2.5 Hz), and 2.76(ddd, 1H, J=13.5, 4.5, and 2.0 Hz). ^{13}C NMR ($CDCl_3$) δ=8.25(q), 20.91(q), 21.63(q), 24.30(t), 28.74(t), 34.50(t), 44.92(t), 103.96 (s), 122.67(s), 158.05(s), 168.37(s), and 171.48(s). Found: m/z 224.1050. Calcd for $C_{12}H_{16}O_4$: M, 224.1048.

3,6-Dimethyl-5,6-dihydrobenzofuran-2(4*H*)-one (10): According to the general procedure C, 231 mg (1.03 mmol) of **9** was treated with acid to give 142 mg (84%) of **10**. IR (neat) 2950, 1765, 1655, 1430, 1290, 1045, and 1002 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.15(d, 3H, J=7.2 Hz), 1.35—2.30(m, 5H), 1.82(s, 3H), and 5.47(d, 1H, J=4.0 Hz). ^{13}C NMR ($CDCl_3$) δ= 8.38(q), 21.15(q), 21.61(t), 29.76(d), 30.93(t), 114.11(d), 119.69(s), 148.20(s), 149.14(s), and 171.56(s). Found: m/z 164.0818. Calcd for $C_{10}H_{12}O_2$: M, 164.0836.

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