A Two Steps Synthesis of γ-Substituted and γ,γ-Disubstituted α-(Alkylmethylene)-γ-butyrolactones

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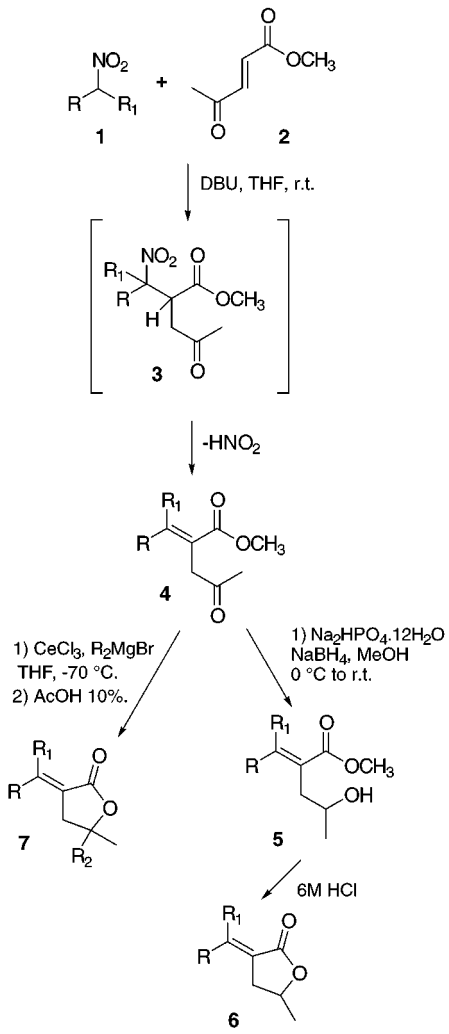
γ-Butyrolactones are an important class of compounds, because they may be easily transformed into butenolides, furans, cyclopentenones, etc.[1] The lactone moiety is also present in many natural products,[2] expecially insect pheromones,[3] antifungal substances, and flavor components or occurs in the essential oils of plants.[4]

Recently there has been an increasingly large amount of research devoted to develop synthetic routes to polysubstituted γ-butyrolactones, in particular of α-methylene-γ-butyrolactones.[5] This has been due in large part to the interest in several biologically active natural products, which have the α-methylenelactone moiety as a major structural feature.[6−10]

Although several methods are available for the synthesis of α-methylene-γ-butyrolactones,[11] the utility of these methods suffer from certain drawbacks such as restricted generality, the need for tedious procedures, and/or expensive chemicals. Much attention has been focused on the synthesis of α-methylene unit from α-phosphono-γ-butyrolactones,[12] but their synthesis requires multisteps sequence, high temperature, and α-halo-γ-lactones as starting material, and some of these are not easily available.[13]

Scheme 1



In the course of our program to explore the novel utilities of functionalized nitroalkanes in the Michael reaction,[14] we disclosed that the nitro group may, simultaneously, behave both as an electron-withdrawing and as a leaving group.[15] Herein we report that γ-alkyl and γ,γ-dialkyl-α-(alkylmethylene)-γ-lactones **6** and **7**, respectively, can be conveniently prepared, in two steps, starting from nitroalkanes **1** and the commercially available methyl *trans*-4-oxo-2-pentenoate **2** (Scheme 1).

It is well know that Michael addition of nitroalkanes to enones can be catalyzed by bases.[16] We have thought to carry out the regiospecific conjugated addition of the nitro compound **1** to methyl *trans*-4-oxo-2-pentenoate **2** in THF using DBU as base. We found that reaction at room-temperature results in full conversion and gives satisfactory yields of the Michael adducts **4** (Table 1) after

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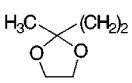
Table 1. Synthesis of Enones 4 and Lactones 6

entry	R	R_1	Nitroalkane	Product **4** (Yield %)[a]	Product **6** (Yield %)[a]
1	C_6H_5	H	**1a**	**4a** (70)	**6a** (70)
2	$C_6H_5CH_2$	H	**1b**	**4b** (78)	**6b** (75)
3	CH_3	CH_3	**1c**	**4c** (87)	**6c** (55)
4	-$(CH_2)_5$-		**1d**	**4d** (71)	**6d** (85)
5	$CH_3(CH_2)_2$	H	**1e**	**4e** (78)	**6e** (67)
6	C_2H_5	H	**1f**	**4f** (93)	**6f** (77)
7	$CH_3O_2C(CH_2)_2$	H	**1g**	**4g** (95)	**6g** (80)
8	$CH_3CH(OH)(CH_2)_2$	H	**1h**	**4h** (85)	**6h** (87)
9		H	**1i**	**4i** (84)	**6i** (70)[b]
10	$CH_3(CH_2)_3$	H	**1j**	**4j** (80)	–

[a]All yields refer to isolated chromatographically pure compounds. [b]Cleavage of acetal moiety.

elimination of nitrous acid from the adduct **3**. The *E*-isomers of the keto esters **4** were highly predominant (up to 93%, determined by NMR analysis of the crude reaction mixture), and this facilitates their purification. It is well documented, in fact, that a β-alkyl substituent *syn* to a carbonyl moiety in α,β-conjugated enones resonates downfield relative to the *anti* alkyl substituent in the NMR spectrum.[17] Consequently, the NMR chemical shifts of the β-methylene or γ-methylene protons, or β-methylene or γ-methine protons of β-secondary alkyl substituents, provide a reliable guide for the assignment of the olefin configuration. The readily available methyl 2-(alkylmethylene)-4-oxopentenoates **4** react with sodium borohydride in the presence of a catalytic amount (12.5 mol %) of sodium hydrogenphosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) to provide γ-hydroxy carboxylates **5**. However, no attempt to isolate these intermediates is undertaken. Instead, treatment with acid during the workup, directly, affords the α-(alkylmethylene)-γ-methyl-γ-lactones **6**. Under these conditions the carbon−carbon double bond was preserved and the lactonization occurred in satisfactory to good yields (Table 1). It should be emphasized that the presence of other functionalities such as the ester (entry 7, Table 1) or hydroxyl group (entry 8, Table 1: in this case any other lactones different from the γ-ones are not observed) are preserved. However, in the case of 2-(alkylmethylene)-4-oxopentenoate contains an acetal moiety **4i** the hydrolysis occurs to the parent ketone, during the acidic workup, to afford the lactone **6i** in good yield (70%).

We also examined the reaction of methyl 2-(alkylmethylene)-4-oxopentenoates **4** with Grignard reagents as nucleophiles.[18] To control the chemoselectivity the reactions were executed at low temperature (−70 °C) and with only a very slight excess of the Grignard reagent. Nevertheless, yields were rarely good under these conditions, and this result is probably due to competing additions of the Grignard reagents to the ester function of **4** or, above all, to the rapid deprotonation of the active methylene hydrogens, leading, after quenching, to the unchanged starting material. On the other hand, adding the keto esters **4** to a suspension of dry cerium(III) chloride[19] in THF, followed by subsequent addition of the organomagnesium reagents at low temperature (−70 °C), results in the selective addition of the organometallic species to the ketone functionality,[20] and the usual workup with acidic quenching gives the γ,γ-dialkyl-α-(alkylmethylene)-γ-butyrolactones **7** in satisfactory yields (Table 2). The success of this strategy can be attributed to the important role that cerium(III) chloride plays in increasing the nucleophilicity and decreasing the basicity of the Grignard reagents.[21]

Table 2. Synthesis of γ,γ-Dialkyl-α-(alkylmethylene)-γ-lactones 7

entry	R	R_1	R_2	Substrate	Product	Yield (%)[a] of **7**
1	$CH_3(CH_2)_3$	H	CH_3	**4j**	**7a**	51
2	$CH_3(CH_3)_3$	H	$CH_3(CH_2)_2$	**4j**	**7b**	52
3	$CH_3(CH_2)_3$	H	$PhCH_2$	**4j**	**7c**	50
4	C_6H_5	H	$CH_3(CH_2)_2$	**4a**	**7d**	53
5	-$(CH_2)_5$-		CH_3	**4d**	**7e**	75
6	-$(CH_2)_5$-		$PhCH_2$	**4d**	**7f**	52
7	CH_3	CH_3	CH_3	**4c**	**7g**	65
8	CH_3	CH_3	$PhCH_2$	**4c**	**7h**	57
9	$CH_3(CH_2)_2$	H	$PhCH_2$	**4e**	**7i**	65

[a]All yields refer to isolated chromatographically pure compounds.

In summary, we have developed a new alternative way for the synthesis of γ-substituted α-(alkylmethylene)-γ-butyrolactones with one more functional group (ester, hydroxyl, and ketone), and, since a wide range of procedures for their transformation into other functionalities is available, their presence in the molecule provides important chances for further elaborations. Thus, the mild reaction conditions and the use of easily available reagents render this method synthetically useful.

Experimental Section

General. All ^1H NMR spectra were collected on a 200 MHz NMR spectrometer in $CDCl_3$. All mass spectra were determined on a HP5890 Series II capillary GC operating in split mode with helium carrier gas and fitted with a mass selective detector (MSD). The column used was a HP5 capillary column 30 m × 0.25 mm, with 0.25 μm film thickness of 5% phenylmethylsilicone gum. The temperature program used the initial temperature of 65 °C for 3 min and then ramped at 15 °C min^{-1} to 280 °C. The products were purified by flash chromatography[22] on Merck silica gel (0.040−0.063 mm). Methyl *trans*-4-oxo-2-pentenoate **2** was purchased from Fluka. The Grignard reagents

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were purchased (Aldrich) as solutions in the corresponding solvent and used as received, and they were titrated before use according to the ref 23. The nitroalkanes **1** were commercially available or prepared by reported procedures.[24]

General Procedure for the Conjugate Addition of Nitroalkanes (1) to Methyl *trans*-4-Oxo-2-pentenoate (2). To a solution of nitroalkane **1** (20 mmol) and methyl *trans*-4-oxo-2-pentenoate **2** (2.56 g, 20 mmol) in THF (70 mL) was added DBU (3.04 g, 20 mmol) at room temperature. After stirring for 3 h and evaporation of the solvent, the crude product was purified by flash chromatography, affording the pure compound **4**.

Methyl (*E*)-2-(2-Oxopropyl)-3-phenylprop-2-enoate (4a): IR (film) 1711, 1640 cm^{-1}; ^1H NMR δ 2.25 (s, 3H), 3.62 (s, 2H), 3.80 (s, 3H), 7.22−7.42 (m, 5H), 7.92 (s, 1H). Anal. Calcd for $C_{13}H_{14}O_3$ C, 71.54; H, 6.46. Found: C, 71.64; H, 6.39.

Methyl (*E*)-2-(2-Oxopropyl)-4-phenylbut-2-enoate (4b): IR (film) 1716, 1649 cm^{-1}; ^1H NMR δ 2.2 (s, 3H), 2.65−2.75 (dd, 1H, J = 4.8 and 17.9 Hz), 3.05−3.2 (m, 1H), 3.45−3.55 (m, 2H), 3.7 (s, 3H), 7.1−7.4 (m, 6H). Anal. Calcd for $C_{14}H_{16}O_3$ C, 72.39; H, 6.94. Found: C, 72.46; H, 6.88.

Methyl 3-Methyl-2-(2-oxopropyl)but-2-enoate (4c): IR (film) 1718, 1650 cm^{-1}; ^1H NMR δ 1.75 (s, 3H), 2.12 (s, 3H), 2.2 (s, 3H), 3.45 (s, 2H), 3.72 (s, 3H). Anal. Calcd for $C_9H_{14}O_3$ C, 63.51; H, 8.29. Found: C, 63.47; H, 8.37.

Methyl 2-Cyclohexylidene-4-oxopentanoate (4d): IR (film) 1718, 1632 cm^{-1}; ^1H NMR δ 1.52−1.62 (m, 8H), 2.08−2.21 (m, 2H), 2.18 (s, 3H), 2.6−2.7 (m, 2H), 3.45 (s, 2H), 3.71 (s, 3H). Anal. Calcd for $C_{12}H_{18}O_3$ C, 68.55; H, 8.63. Found: C, 68.47; H, 8.67.

Methyl (*E*)-2-(2-Oxopropyl)hex-2-enoate (4e): IR (film) 1713, 1640 cm^{-1}; ^1H NMR δ 0.92 (t, 3H, J = 7.3 Hz), 1.38−1.58 (m, 2H), 2.02−2.2 (m, 2H), 2.18 (s, 3H), 3.41 (s, 2H), 3.71 (s, 3H), 6.98 (t, 1H, J = 7.5 Hz). Anal. Calcd for $C_{10}H_{16}O_3$ C, 65.19; H, 8.75. Found: C, 65.27; H, 8.67.

Methyl (*E*)-2-(2-Oxopropyl)pent-2-enoate (4f): IR (film) 1713, 1650 cm^{-1}; ^1H NMR δ 1.05 (t, 3H, J = 7.5 Hz), 2.05−2.15 (m, 2H), 2.2 (s, 3H), 3.4 (s, 2H), 3.7 (s, 3H), 6.95 (t, 1H, J = 7.5 Hz). Anal. Calcd for $C_9H_{14}O_3$ C, 63.51; H, 8.29. Found: C, 63.58; H, 8.27.

Dimethyl (*E*)-2-(2-Oxopropyl)hex-2-enedioate (4g): IR (film) 1717, 1649 cm^{-1}; ^1H NMR δ 2.2 (s, 3H), 2.4−2.5 (m, 4H), 3.4 (s, 3H), 3.67 (s, 3H), 3.71 (s, 3H), 6.96−7.00 (m, 1H). Anal. Calcd for $C_{11}H_{16}O_5$ C, 57.88; H, 7.07. Found: C, 57.95; H, 7.02.

Methyl (*E*)-6-Hydroxy-2-(2-oxopropyl)hept-2-enoate (4h): IR (film) 3430, 1712, 1650 cm^{-1}; ^1H NMR δ 1.18 (d, 3H, J = 6.2 Hz), 1.5−1.6 (m, 2H), 2.2 (s, 3H), 2.18−2.35 (m, 2H), 3.45 (s, 2H), 3.7 (s, 3H), 3.7−3.8 (m, 1H), 6.95 (t, 1H, J = 7.6 Hz). Anal. Calcd for $C_{11}H_{19}O_4$ C, 61.37; H, 8.90. Found: C, 61.42; H, 8.87.

Methyl (*E*)-5-(2-Methyl-1,3-dioxolan-2-yl)-2-(2-oxopropyl)pent-2-enoate (4i): IR (film) 1712, 1649 cm^{-1}; ^1H NMR δ 1.3 (s, 3H), 1.68−1.7 (m, 2H), 2.2 (s, 3H), 2.12−2.26 (m, 2H), 3.44 (s, 2H), 3.72 (s, 3H), 3.86−3.98 (m, 4H), 7.00 (t, 1H, J = 7.5 Hz). Anal. Calcd for $C_{14}H_{22}O_5$ C, 62.20; H, 8.20. Found: C, 62.27; H, 8.27.

Methyl (*E*)-2-(2-Oxopropyl)hept-2-enoate (4e): IR (film) 1713, 1640 cm^{-1}; ^1H NMR δ 0.92 (t, 3H, J = 7.3 Hz), 1.38−1.6 (m, 4H), 2.02−2.2 (m, 2H), 2.18 (s, 3H), 3.41 (s, 2H), 3.71 (s, 3H), 6.98 (t, 1H, J = 7.5 Hz). Anal. Calcd for $C_{11}H_{18}O_3$ C, 66.63; H, 9.15. Found: C, 66.77; H, 9.07.

General Procedure for Preparing α-(Alkylmethylene)-γ-methyl-γ-lactones (6). To a cooled (0 °C) solution of compound **4** (1.5 mmol) in MeOH (10 mL) were consecutively added $Na_2HPO_4 \cdot 12H_2O$ (0.067 g, 0.188 mmol) and $NaBH_4$ (0.057 g, 1.5 mmol). The mixture was stirred for 2 h at 0 °C and then at room temperature for 10 h. The mixture was then acidified to pH 1−2 with 6 M HCl, extracted with Et_2O (3 × 10 mL), dried ($MgSO_4$), and evaporated to give the crude lactone. Further purification by flash chromatography afforded the pure compound **6**.

5-Methyl-3-[(*E*)-phenylmethylidene]dihydrofuran-2(*3H*)-one (6a): IR (film) 3057, 1747, 1651 cm^{-1}; ^1H NMR δ 1.45 (d, 3H, J = 6.3 Hz), 2.72−2.9 (m, 1H), 3.3−3.5 (m, 1H), 4.68−4.85 (m, 1H), 7.4−7.6 (m, 6H); EIMS (70 eV) m/z 188 [M^+], 159, 128, 116, 77, 63, 51. Anal. Calcd for $C_{12}H_{12}O_2$ C, 76.57; H, 6.43. Found: C, 76.67; H, 6.47.

5-Methyl-3-[(*E*)-phenylethylidene]dihydrofuran-2(*3H*)-one (6b): IR (film) 2977, 1751, 1679 cm^{-1}; ^1H NMR δ 1.45 (d, 3H, J = 6.2 Hz), 2.4−2.6 (m, 1H), 3.0−3.2 (m, 1H), 3.50 (d, 2H, J = 7.7 Hz), 4.5−4.8 (m, 1H), 6.45−6.55 (m, 1H), 7.1−7.4 (m, 4H); EIMS (70 eV) m/z 202 [M^+], 143, 129, 91, 77. Anal. Calcd for $C_{13}H_{14}O_2$ C, 72.20; H, 6.98. Found: C, 72.17; H, 6.97.

5-Methyl-3-(1-methylethylidene)dihydrofuran-2(*3H*)-one (6c): IR (film) 2930, 1742, 1667 cm^{-1}; ^1H NMR δ 1.35 (d, 3H, J = 6.2 Hz), 1.8 (s, 3H), 2.2 (s, 3H), 2.4−2.5 (m, 1H), 2.9−3.1 (m, 1H), 4.45−4.6 (m, 1H); EIMS (70 eV) m/z 140 [M^+], 125, 107, 79, 68, 41. Anal. Calcd for $C_8H_{12}O_2$ C, 68.54; H, 8.63. Found: C, 68.47; H, 8.67.

3-Cyclohexylidene-5-methyldihydrofuran-2(*3H*)-one (6d): IR (film) 2929, 1741, 1658 cm^{-1}; ^1H NMR δ 1.38 (d, 3H, J = 6.3 Hz), 1.5−1.8 (m, 6H), 2.15−2.25 (m, 2H), 2.43 (dd, 1H, J = 6.2 and 15.2 Hz), 2.9−3.0 (m, 2H), 4.5−4.65 (m, 1H); EIMS (70 eV) m/z 180 [M^+], 135, 107, 79, 41. Anal. Calcd for $C_{11}H_{16}O_2$ C, 73.30; H, 8.95. Found: C, 73.40; H, 8.87.

3-[(*E*)-Butylidene]-5-methyldihydrofuran-2(*3H*)-one (6e): IR (film) 2961, 1754 cm^{-1}; ^1H NMR δ 0.9 (t, 3H, J = 7.1 Hz), 1.4 (d, 3H, 6.2 Hz), 1.4−1.6 (m, 2H), 2.1−2.2 (m, 2H), 2.35−2.5 (m, 1H), 2.9−3.1 (m, 1H), 4.55−4.7 (m, 1H), 6.55−6.75 (m, 1H); EIMS (70 eV) m/z 154 [M^+], 125, 95, 83, 67, 41. Anal. Calcd for $C_9H_{14}O_2$ C, 70.10; H, 9.15. Found: C, 70.04; H, 9.17.

5-Methyl-3-[(*E*)-propylidene]dihydrofuran-2(*3H*)-one (6f): IR (film) 1755, 1681 cm^{-1}; ^1H NMR δ 1.1 (t, 3H, J = 7.5 Hz), 1.4 (d, 3H, J = 6.2 Hz), 2.1−2.25 (m, 2H), 2.3−2.5 (m, 1H), 2.8−3.1 (m, 1H), 4.55−4.75 (m, 1H), 6.6−6.75 (m, 1H); EIMS (70 eV) m/z 140 [M^+], 111, 95, 81, 67, 41. Anal. Calcd for $C_8H_{12}O_2$ C, 68.54; H, 8.63. Found: C, 68.61; H, 8.67.

Methyl 4-[(*E*)-5-Methyl-2-oxodihydrofuran-3(*2H*)-ylidene]-butanoate (6g): IR (film) 2954, 1750, 1683 cm^{-1}; ^1H NMR δ 1.4 (d, 3H, J = 6.2 Hz), 2.35−2.55 (m, 5H), 3.0−3.15 (m, 1H), 3.68 (s, 3H), 4.6−4.75 (m, 1H), 6.65−6.75 (m, 1H); EIMS (70 eV) m/z 198 [M^+], 183, 151, 107, 93, 79, 67. Anal. Calcd for $C_{10}H_{14}O_4$ C, 68.54; H, 8.63. Found: C, 68.61; H, 8.67.

3-[(*E*)-4-Hydroxypentylidene]-5-methyldihydrofuran-2(*3H*)-one (6h): IR (film) 1748, 1711 cm^{-1}; ^1H NMR δ 1.39 (d, 3H, J = 6.2 Hz), 2.15 (s, 3H), 2.3−2.45 (m, 2H), 2.45−2.55 (m, 1H), 2.56−2.65 (m, 2H), 2.38−3.14 (m, 1H), 4.55−4.75 (m, 1H), 6.5−6.6 (m, 1H); EIMS (70 eV) m/z 182 [M^+], 149, 140, 111, 79, 43. Anal. Calcd for $C_{10}H_{14}O_3$ C, 65.19; H, 8.75. Found: C, 65.21; H, 8.67.

5-Methyl-3-[(*E*)-4-oxopentylidene)dihydrofuran-2(*3H*)-one (6i): IR (film) 2954, 1750, 1683 cm^{-1}; ^1H NMR δ 1.4 (d, 3H, J = 6.2 Hz), 2.35−2.55 (m, 5H), 3.0−3.15 (m, 1H), 3.68 (s, 3H), 4.6−4.75 (m, 1H), 6.65−6.75 (m, 1H); EIMS (70 eV) m/z 198 [M^+], 183, 151, 107, 93, 79, 67. Anal. Calcd for $C_{10}H_{14}O_4$ C, 65.91; H, 7.74. Found: C, 65.81; H, 7.67.

General Procedure for Preparing γ,γ-Dialkyl-α-(alkylmethylene)-γ-butyrolactones (7). Finely ground $CeCl_3 \cdot 7H_2O$ (1.5 mmol) was dried by heating at 140 °C/0.1 Torr for 2 h.[25] Dry THF (10 mL) was then added at 0 °C, and the milky suspension was stirred overnight under nitrogen at room temperature. At this temperature, a solution of **4** (1 mmol) in THF (5 mL) was added and left to stir for 1 h. Then, it was cooled to −70 °C, and Grignard reagent (1.5 mmol) was added by syringe. The reaction mixture was then left to stir until TLC indicated that no starting material remained. The reaction was quenched with 10% AcOH and extracted with Et_2O (3 × 10 mL). The ethereal extract was washed with water (2 × 10 mL) and brine

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(25) It has been recently reported (Evans, W. J.; Feldman, J. D.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 4581) that the material obtained after drying of $CeCl_3 \cdot 7H_2O$ (at 150 °C and 0.03 Torr for 12 h) was $[CeCl_3 \cdot (H_2O)]_n$. We have not analyzed the $CeCl_3$ prepared by the present procedure, however, the material was highly efficient without the need of a large excess of Grignard reagent.

(10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography to give the corresponding lactone **7**.

5,5-Dimethyl-3-[(*E*)-pentylidene]dihydrofuran-2(*3H*)-one (7a): IR (film) 1755 cm^{-1}; ^1H NMR δ 0.9 (t, 3H, J = 7.0 Hz), 1.42 (s, 6H), 1.25−1.55 (m, 4H), 2.1−2.2 (m, 2H), 2.7 (s, 2H), 6.65−6.75 (m, 1H); EIMS (70 eV) m/z 182 [M^+], 167, 82, 67, 43. Anal. Calcd for $C_{11}H_{18}O_2$ C, 72.49; H, 9.95. Found: C, 72.51; H, 9.87.

5-Methyl-3-[(*E*)-pentylidene]-5-propyldihydrofuran-2(*3H*)-one (7b): IR (film) 1754 cm^{-1}; ^1H NMR δ 0.85−0.95 (m, 6H), 1.3−1.5 (m, 6H), 1.4 (s, 3H), 1.6−1.7 (m, 2H), 2.1−2.2 (m, 2H), 2.6−2.7 (m, 2H), 6.66−7.66 (m, 1H); EIMS (70 eV) m/z 210 [M^+], 167, 121, 81, 67, 43. Anal. Calcd for $C_{13}H_{22}O_2$ C, 74.24; H, 10.54. Found: C, 74.31; H, 10.47.

5-Benzyl-5-methyl-3-[(*E*)-pentylidene]dihydrofuran-2(*3H*)-one (7c): IR (film) 1753 cm^{-1}; ^1H NMR δ 0.87 (t, 3H, J = 7.0 Hz), 1.2−1.36 (m, 4H), 1.43 (s, 3H), 2.0−2.1 (m, 1H), 2.45−2.85 (m, 2H), 2.86−3.05 (m, 2H), 6.5−6.6 (m, 1H), 7.15−7.3 (m, 5H); EIMS (70 eV) m/z 258, 167, 121, 91, 77, 65, 43. Anal. Calcd for $C_{17}H_{22}O_2$ C, 79.03 H, 8.58. Found: C, 79.11; H, 8.47.

5-Methyl-3-[(*E*)-phenylmethylidene]-5-propyldihydrofuran-2(*3H*)-one (7d): IR (film) 1716 cm^{-1}; ^1H NMR δ 1.02 (t, 3H, J = 7.1 Hz), 1.32 (s, 3H), 1.35−1.50 (m, 3H), 1.63−1.75 (m, 1H), 2.52 (d, 1H, J = 17.05 Hz), 2.74 (d, 1H, J = 17.05 Hz), 7.01−7.09 (m, 2H), 7.26−7.35 (m, 2H), 7.56−7.60 (m, 2H); EIMS (70 eV) m/z 230 [M^+], 215, 187, 91, 82, 77, 43. Anal. Calcd for $C_{15}H_{18}O_2$ C, 78.23; H, 7.88. Found: C, 78.31; H, 7.94.

5,5-Dimethyl-3-[cyclohexylidene]dihydrofuran-2(*3H*)-one (7e): IR (film) 1730 cm^{-1}; ^1H NMR δ 1.4 (s, 6H), 1.55−1.7 (m, 6H), 2.15−2.22 (m, 2H), 2.68 (s, 2H), 2.9−3.0 (m, 2H); EIMS (70 eV) m/z 194 [M^+], 179, 133, 121, 79, 67. Anal. Calcd for $C_{12}H_{18}O_2$ C, 74.19; H, 9.34. Found: C, 74.11; H, 9.24.

5-Benzyl-3-cyclohexylidene-5-methyldihydrofuran-2(*3H*)-one (7f): IR (film) 1765 cm^{-1}; ^1H NMR δ 1.25 (s, 3H), 1.5−1.7 (m, 10H), 2.05−2.15 (m, 2H), 2.2−2.3 (m, 2H), 7.15−7.35 (m, 5H); EIMS (70 eV) m/z 270 [M^+], 151, 107, 91, 77, 43. Anal. Calcd for $C_{18}H_{22}O_2$ C, 79.96; H, 8.20. Found: C, 80.01; H, 8.14.

5,5-Dimethyl-3-(1-methylethylidene)dihydrofuran-2(*3H*)-one (7 g): IR (film) 1740 cm^{-1}; ^1H NMR δ 1.39 (s, 6H), 1.82−1.84 (m, 3H), 2.2−2.8 (m, 3H), 2.62−2.68 (m, 2H); EIMS (70 eV) m/z 154 [M^+], 121, 107, 81, 68, 43. Anal. Calcd for $C_9H_{14}O_2$ C, 70.10; H, 9.15. Found: C, 70.01; H, 9.24.

5-Benzyl-5-methyl-3-(1-methylethylidene)dihydrofuran-2(*3H*)-one (7h): IR (film) 1743 cm^{-1}; ^1H NMR δ 1.4 (s, 3H), 1.73 (s, 3H), 2.11 (s, 3H), 2.48 (d, 1H, J = 12.7 Hz), 2.8 (d, 1H, J = 12.7 Hz), 2.9 (dd, 2H, J = 13.6 and 23.9 Hz), 7.15−7.3 (m, 5H); EIMS (70 eV) m/z 230 [M^+], 215, 139, 111, 91, 77, 67, 43. Anal. Calcd for $C_{15}H_{18}O_2$ C, 78.23; H, 7.88. Found: C, 78.31; H, 7.94.

5-Benzyl-5-methyl-3-[(*E*)-butylidene)dihydrofuran-2(*3H*)-one (7i): IR (film) 1765 cm^{-1}; ^1H NMR δ 0.95 (t, 3H, J = 7.2 Hz), 1.42 (s, 3H), 1.35−1.45 (m, 2H), 1.8−2.0 (m, 2H), 2.36−2.56 (m, 2H), 2.85−3.05 (m, 2H), 6.91−6.98 (m, 1H), 7.12−7.35 (m, 5H); EIMS (70 eV) m/z 244 [M^+], 153, 125, 111, 91, 77, 65, 43. Anal. Calcd for $C_{11}H_{20}O_2$ C, 72.49; H, 9.95. Found: C, 72.41; H, 10.01.

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