Nickel- and Palladium-Catalyzed Aldol-Type Condensation by Enol Esters

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$PdCl_2(PhCN)_2$–$SnCl_2$, bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$]/PPh_3–Zn, $NiBr_2(PPh_3)_2$–Zn, or $Pd(OAc)_2$/PPh_3–Zn catalytic systems induced aldol-type condensation of isopropenyl acetate with aldehydes to produce 4-substituted (*E*)-3-buten-2-ones. $PdCl_2(PhCN)_2$–$SnCl_2$ was utilized in the aldol-type reaction with any arenecarbaldehyde, bearing either an electron-donating group or an electron-withdrawing group, at 50 °C in acetonitrile. Catalytic systems using zinc, in particular $Ni(cod)_2$/PPh_3–Zn, exhibited some high chemoselectivities at 60 °C in dioxane: (1) an aldehyde only reacted in the presence of an internal ester or ketone, (2) olefinic aldehydes only reacted in the presence of saturated aliphatic aldehydes, (3) reactivity in the condensation with substituted benzaldehydes is the inverse of that in usual nucleophilic addition to carbonyl compound, and (4) 2-methoxybenzaldehyde only reacted in the presence of 4-methoxybenzaldehyde. Using $PdCl_2(PhCN)_2$–$SnCl_2$, $Ni(cod)_2$/PPh_3–Zn, or $Pd(OAc)_2$/PPh_3–Zn, cyclic enol ester, namely 5-methyl-2(3*H*)-furanone also caused aldol-type reaction with carbonyl compounds. The reaction with $Ni(cod)_2$/PPh_3–Zn or $Pd(OAc)_2$/PPh_3–Zn at 60 °C in dioxane selectively produced 5-substituted 4-acetyl-2(5*H*)-furanones via dehydrogenation of γ-substituted β-acetyl-γ-butyrolactones.

Oxidative addition/reductive elimination in organometallic chemistry is one of the most important routes for organic synthesis.[1] One application of oxidative addition/reductive elimination of esters to organic synthesis is palladium-catalyzed allylic alkylation[2] or carbonyl allylation.[3] Each is caused by the oxidative addition of allylic esters to palladium(0) complexes, accompanied by the cleavage of an alkyl-oxygen bond of an ester group. Oxidative addition accompanied by the cleavage of acyl-oxygen bond has only occurred in aryl esters.[4] No oxidative addition of acyl-oxygen bond in ester group to metal complex has been applied to organic synthesis. Enol esters, which are easily prepared and are tractable as nucleophiles, have been applied to aldol-type condensation utilizing the cleavage of acyl-oxygen bond in the enol esters under basic conditions[5] and acidic conditions.[6] We hoped that oxidative addition of enol ester to metal(0) complex, accompanied by the cleavage of acyl-oxygen bond, would lead to formation of oxaallylmetal complex (metal enolate),[7,8] which could be applied to aldol-type condensation under neutral conditions. We here report nickel- or palladium-catalyzed aldol-type condensation by enol esters with reducing agents via the formation of oxaallylnickel or -palladium complexes.[9]

Results and Discussion

Aldol-Type Condensation by Isopropenyl Acetate. $PdCl_2(PhCN)_2$–$SnCl_2$ reagent, which was used in the carbonyl allylation by allylic alcohol via oxidative addition/reductive elimination,[3] was found to be effective for the aldol-type condensation of isopropenyl acetate (**1**) and aldehydes **2** at 50 °C in acetonitrile under a nitrogen atmosphere to produce (*E*)-3-buten-2-ones **3**. The results are summarized in Table 1. The reaction occurred without $PdCl_2(PhCN)_2$ (Entry 3) and did not occur without $SnCl_2$. The addition of a catalytic amount of $PdCl_2(PhCN)_2$ accelerated the reaction (Entry 2). Phosphine, phosphite, or arsine ligands were not effective for the catalytic activity of palladium (Entries 5—8). The reaction did not occur at 30 °C (Entry 1), while at 80 °C, the yield of **3** (R=4-$MeO_2CC_6H_4$) was low and many undetermined by-products were produced (Entry 4). SnF_2 and $SnBr_2$, instead of $SnCl_2$, were not effective for the aldol-type condensation. Polar solvents such as THF, DMF, and 1,3-dimethyl-2-imidazolidinone (DMI) were not available for the reaction under the same conditions as those in DMSO shown in Entry 9. The aldol-type condensation of **1** and any aromatic aldehyde, bearing either an electron-donating group or an electron-withdrawing group, in acetonitrile proceeded selectively to produce (*E*)-4-aryl-3-buten-2-ones **3** in good yields (Entries 2 and 10—16), in contrast with the reaction of **1** and benzaldehyde with Lewis acids.[6a] Aliphatic aldehydes such as heptanal and cyclohexanecarbaldehyde did not contribute so much to the aldol-type reaction, and aliphatic aldehydes bearing functional groups such as C=C double bond and aryl were converted to **3** [R=$PhCH{=}CH$, $PhCH_2CH_2$, $CH_2{=}CH(CH_2)_8$] only in very small yields (Entries 17—19).

When we used bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$], $NiBr_2(PPh_3)_2$, or $Pd(OAc)_2$ as a catalyst, the aldol-type condensation by **1** did not proceed with $SnCl_2$ in acetonitrile, but with zinc in dioxane it did proceed to produce (*E*)-3-buten-2-ones **3**. The results are summarized in Table 2. The aldol-type condensation of **1** and benzaldehyde with $Ni(cod)_2$–Zn was investigated under various conditions. The condensation with $Ni(cod)_2$/$2PPh_3$–Zn at 60 °C smoothly proceeded in dioxane (Entry 1), and was very difficult in ether, THF, acetonitrile, DMF, or DMI. The condensation with $Ni(cod)_2$/$2PPh_3$–Zn in dioxane did not occur below 40 °C, and produced many unidentifiable by-

Table 1. Palladium-Catalyzed Aldol-Type Condensation of **1** and **2** with $SnCl_2$[a)]

1 **2** **3**

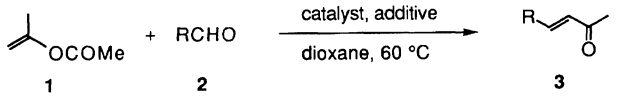
Entry	R	Ligand[b)]	Temp/°C	Time/h	Yield/%[c)]
1	4-$MeO_2CC_6H_4$	—	30	48	Trace
2	4-$MeO_2CC_6H_4$	—	50	33	88
3	4-$MeO_2CC_6H_4$	—	50	72	45[d)]
4	4-$MeO_2CC_6H_4$	—	80	48	56
5	4-$MeO_2CC_6H_4$	P(*n*-Bu)$_3$	50	48	48
6	4-$MeO_2CC_6H_4$	PPh_3	50	48	58
7	4-$MeO_2CC_6H_4$	$P(OMe)_3$	50	48	65
8	4-$MeO_2CC_6H_4$	$AsPh_3$	50	48	70
9	4-$MeO_2CC_6H_4$	—	50	48	28[e)]
10	C_6H_5	—	50	48	58
11	3,4-$(CH_2O_2)C_6H_3$	—	50	40	78
12	2-$MeOC_6H_4$	—	50	30	79
13	4-$O_2NC_6H_4$	—	50	40	82
14	4-NCC_6H_4	—	50	35	92
15	4-ClC_6H_4	—	50	33	83
16	3-$OHCC_6H_4$	—	50	40	53[f)]
17	PhCH=CH	—	50	35	28
18	$PhCH_2CH_2$	—	50	32	18
19	CH_2=CH$(CH_2)_8$	—	50	30	32

a) The reaction of **1** (3 mmol) and **2** (1 mmol) with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (3 mmol) was carried out in acetonitrile (5 ml) under a nitrogen atmosphere. b) Ligand (0.04 mmol) was used. c) Isolated Yields (>95% *E*-isomer) based on **2**. d) No palladium catalyst was added. e) DMSO was used as a solvent. f) 1,3-Bis(3-oxo-1-butenyl)benzene was obtained.

products over 80 °C. PPh_3 (52%) was a better ligand than P(*n*-Bu)$_3$ (27%), bis(diphenylphosphino)methane (30%), bis(diphenylphosphino)ethane (40%), bis(diphenylphosphino)propane (25%), $P(OMe)_3$ (45%), $P(OPr^i)_3$ (26%), $P(OPh)_3$ (42%), $AsPh_3$ (47%), or $SbPh_3$ (20%) in the condensation with $Ni(cod)_2$–Zn at 60 °C in dioxane for 4 d (Entry 1). A procedure using PPh_3 (two equimolar amounts to Ni catalyst) as a ligand at 60 °C in dioxane was found to exhibit the best result of the aldol-type condensation with $Ni(cod)_2$–Zn (Entry 2). Prolongation of reaction time enhanced the yield of **3** (R=C_6H_5); $Ni(cod)_2$ (10 mol%), PPh_3 (20 mol%), 7 d, 80%. The aldol-type condensation of **1** and various aldehydes **2** with $Ni(cod)_2$–Zn, $NiBr_2(PPh_3)_2$–Zn, or $Pd(OAc)_2$–Zn was carried out under the same conditions as the best for that of **1** and benzaldehyde. Aromatic aldehydes (Entries 1, 2, 5—8, 11, and 12) and aliphatic aldehydes bearing an aryl group (Entries 16 and 17), a C=C double bond (Entries 19, and 22—28), a methoxycarbonyl group (Entry 29), or an oxo group (Entry 30) were converted to the corresponding (*E*)-3-buten-2-ones **3** stereoselectively. Those catalytic systems are better than $PdCl_2(PhCN)_2$–$SnCl_2$ system in the condensation with the aliphatic aldehydes. The reaction of (*E*)-cinnamaldehyde with **1** afforded a (*Z*)-α, β-unsaturated ketone, namely (3*Z*,5*E*)-6-phenyl-3,5-hexadien-2-one (Entries 13—15), and its stereoselectivity (>97% *Z*-isomer) was opposite to that (>95% *E*-isomer) in the $PdCl_2(PhCN)_2$–$SnCl_2$ system (Entry 17, Table 1). Aldehydes, bearing coordinating groups such as electron-rich arene, alkene, ester and ketone, were found to be available for this reaction. The condensation by **1** with $Ni(cod)_2/PPh_3$–Zn thus exhibited some high chemoselectivities: (1) an aldehyde only condensed with **1** in the presence of an internal ester or ketone (Entries 29 and 30 in Table 2), (2) olefinic aldehydes only reacted in the presence of saturated aliphatic aldehydes (Entries 1 and 2 in Table 3), (3) reactivity in the condensation with substituted benzaldehydes is the inverse of that in usual nucleophilic addition to carbonyl compound (Entry 3 in Table 3), and (4) 2-methoxybenzaldehyde only reacted in the presence of 4-methoxybenzaldehyde (Entry 4 in Table 3).

The aldol-type reaction by **1** with $PdCl_2(PhCN)_2$–$SnCl_2$ might be promoted either by the coordination of carbonyl oxygen of aldehydes **2** to $Pd(SnCl_3)_2(PhCN)_2$[10)] derived from $PdCl_2(PhCN)_2$ and $SnCl_2$ or by the oxidative addition of **1** to palladium complex, accompanied by the cleavage of acyl-oxygen bond, followed by the transmetallation of palladium enolate into tin enolate.[11,12)] The oxidative addition of **1** to palladium seems to have higher possibility than the coordination of **2** to $Pd(SnCl_3)_2(PhCN)_2$, since dimethyl acetals of **2** do not react with **1** under the same conditions as those shown in Table 1.[13)] However, the aldol-type reaction is unavoidable due to the participation

Table 2. Nickel- or Palladium-Catalyzed Aldol-Type Condensation by **1**[a)]

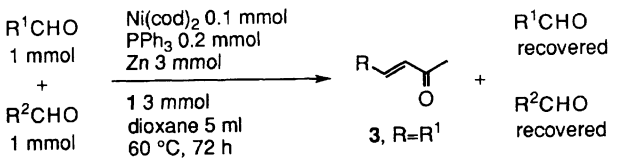


1 2 3

Entry	R	Catalyst (mol%)[b)]	Additive	Time/d	Yield/%[c)]
1	C_6H_5	$Ni(cod)_2/2PPh_3$(2)	Zn	4	52
2	C_6H_5	$Ni(cod)_2/2PPh_3$(10)	Zn	3	68
3	C_6H_5	$Ni(cod)_2/2PPh_3$(10)	$NaHCO_3$	3	53
4	C_6H_5	$Ni(cod)_2/2PPh_3$(10)	CsF	3	49
5	C_6H_5	$NiBr_2(PPh_3)_2$(20)	Zn	4	50
6	C_6H_5	$Pd(OAc)_2/2PPh_3$(4)	Zn	4	55
7	C_6H_5	$Pd(OAc)_2/2PPh_3$(10)	Zn	4	65
8	2-$CH_3OC_6H_4$	$Ni(cod)_2/2PPh_3$(10)	Zn	2	62
9	2-$CH_3OC_6H_4$	$Ni(cod)_2/2PPh_3$(10)	$NaHCO_3$	3	65
10	2-$CH_3OC_6H_4$	$Ni(cod)_2/2PPh_3$(10)	CsF	3	60
11	2-$CH_3OC_6H_4$	$NiBr_2(PPh_3)_2$(20)	Zn	5	53
12	2-$CH_3OC_6H_4$	$Pd(OAc)_2/2PPh_3$(10)	Zn	4	59
13	(*E*)-C_6H_5CH=CH	$Ni(cod)_2/2PPh_3$(10)	Zn	3	48[d)]
14	(*E*)-C_6H_5CH=CH	$NiBr_2(PPh_3)_2$(20)	Zn	4	35[d)]
15	(*E*)-C_6H_5CH=CH	$Pd(OAc)_2/2PPh_3$(10)	Zn	4	44[d)]
16	$C_6H_5CH_2CH_2$	$Ni(cod)_2/2PPh_3$(10)	Zn	3	55
17	$C_6H_5CH_2CH_2$	$NiBr_2(PPh_3)_2$(20)	Zn	4	38
18	$C_6H_5CH_2CH_2$	$Pd(OAc)_2/2PPh_3$(10)	Zn	3	55
19	CH_2=$CH(CH_2)_8$	$Ni(cod)_2/2PPh_3$(10)	Zn	3	65
20	CH_2=$CH(CH_2)_8$	$Ni(cod)_2/2PPh_3$(10)	$NaHCO_3$	3	42
21	CH_2=$CH(CH_2)_8$	$Ni(cod)_2/2PPh_3$(10)	CsF	3	38
22	CH_2=$CH(CH_2)_8$	$NiBr_2(PPh_3)_2$(20)	Zn	4	68
23	CH_2=$CH(CH_2)_8$	$Pd(OAc)_2/2PPh_3$(10)	Zn	3	75
24	Me_2C=$CH(CH_2)_2CHMeCH_2$	$Ni(cod)_2/2PPh_3$(10)	Zn	3	80
25	Me_2C=$CH(CH_2)_2CHMeCH_2$	$NiBr_2(PPh_3)_2$(20)	Zn	4	75
26	Me_2C=$CH(CH_2)_2CHMeCH_2$	$Pd(OAc)_2/2PPh_3$(10)	Zn	3	85
27	3-Cyclohexenyl	$Ni(cod)_2/2PPh_3$(10)	Zn	3	58
28	3-Cyclohexenyl	$NiBr_2(PPh_3)_2$(20)	Zn	4	52
29	$CH_3O_2C(CH_2)_8$	$Ni(cod)_2/2PPh_3$(10)	Zn	3	58
30	$CH_3CO(CH_2)_8$	$Ni(cod)_2/2PPh_3$(10)	Zn	3	48

a) The reaction of **1** (3 mmol) and **2** (1 mmol) with catalyst and additive (3 mmol) was carried out at 60 °C in dioxane (5 ml) under a nitrogen atmosphere. b) Mol% based on aldehydes. c) Isolated yields (>97% *E*-isomer). Yields based on the consumed aldehydes were 83—91%. d) (3*Z*,5*E*)-6-Phenyl-3,5-hexadien-2-one was obtained.

Table 3. Chemoselection in Nickel-Catalyzed Aldol-Type Condensation by **1**



Entry	Aldehyde		**3** (R=R^1)	Recovered aldehyde	
	R^1	R^2	Yield/%[a)]	R^1%[a)]	R^2%[a)]
1	3-Cyclohexenyl	*c*-C_6H_{11}	68	10	89
2	H_2C=$CH(CH_2)_8$	$CH_3(CH_2)_9$	62	14	83
3	C_6H_5	4-NCC_6H_4	60	18	95
4	2-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	63	28	92

a) Isolated yields (**3**; >97% *E*-isomer).

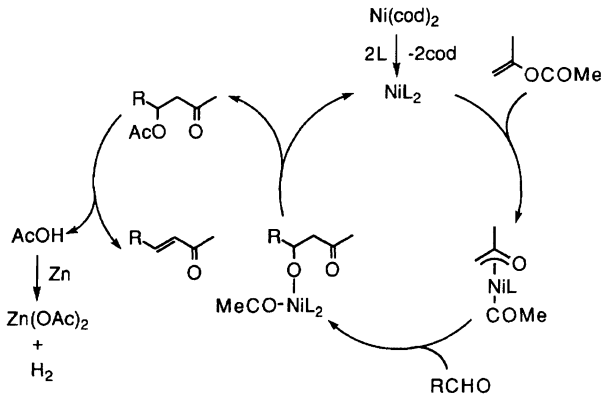
of a Lewis acid, $Pd(SnCl_3)_2(PhCN)_2$. The catalytic activity of $Ni(cod)_2/PPh_3$–Zn and $Pd(OAc)_2/PPh_3$–Zn, having no Lewis acidity, may deny the coordination of aldehydes **2** to Ni or Pd, and may support the oxidative addition of **1** to Ni or Pd accompanied by the cleavage of acyl-oxygen bond. The reaction using an amount of $Ni(cod)_2/2PPh_3$ equimolar to that of **2** [R=C_6H_5, CH_2=$CH(CH_2)_8$], without zinc, produced **3** (R=C_6H_5, 42%; R=CH_2=$CH(CH_2)_8$, 58%] at 60 °C for 24 h, in contrast with $NiBr_2(PPh_3)_2$ and $Pd(OAc)_2/2PPh_3$.

Acetic acid, which was apparently eliminated, was actually trapped as zinc acetate which was identified with commercially available $Zn(OAc)_2 2H_2O$ by IR. In the use of only fresh $Ni(cod)_2$, the condensation proceeded with bases such as $NaHCO_3$ and CsF instead of Zn (Entries 3, 4, 9, 10, 20, and 21 in Table 2).[14] $NaHCO_3$ and CsF were not effective for the condensation with $NiBr_2(PPh_3)_2$ and $Pd(OAc)_2/2PPh_3$. These results suggest that the $Ni(cod)_2$-catalyzed reaction is caused by the oxidative addition of **1** to Ni(0), accompanied by the acyl-oxygen cleavage, namely the formation of oxaallylnickel complex, followed by the nucleophilic addition of the oxaallylnickel (or nickel enolate) to an aldehyde coordinating to Ni(0), as illustrated in Scheme 1. This $NiBr_2(PPh_3)_2$-catalyzed reaction should require zinc to reduce Ni(II) to Ni(0). A palladium-catalyzed reaction probably proceeds not via the transmetallation of oxaallylpalladium complex, having no nucleophilicity, into zinc enolate but via electron transfer from zinc to oxaallylpalladium complex,[15] because the palladium-catalyzed reaction needs zinc and is only applicable to aldehydes bearing coordinating groups similarly to the nickel-catalyzed reaction. And its actual nucleophile may be the reduced state of oxaallylpalladium complex.

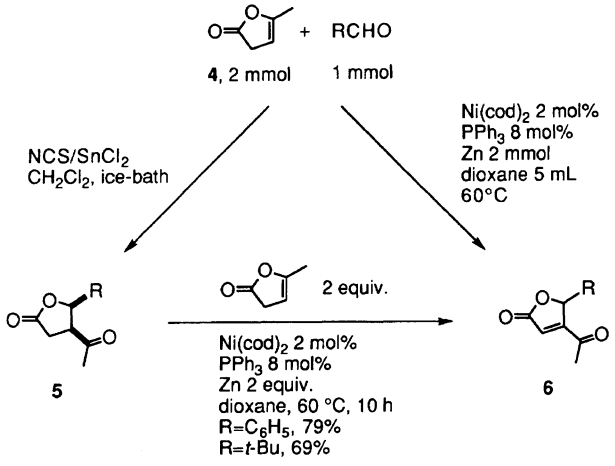
Aldol-Type Condensation/Dehydrogenation of 5-Methyl-2(3*H*)-furanone. The aldol-type reaction of cyclic enol ester, 5-methyl-2(3*H*)-furanone (**4**) was carried out with three kinds of catalytic systems: $PdCl_2(PhCN)_2$–$SnCl_2$, $Ni(cod)_2/PPh_3$–Zn, and $Pd(OAc)_2/PPh_3$–Zn. The results are summarized in Table 4. In the reaction of **4** with $PdCl_2(PhCN)_2$–$SnCl_2$ at 50 °C in acetonitrile, aromatic aldehydes were converted to *cis*-*β*-acetyl-*γ*-aryl-*γ*-butyrolactones **5** (Entries 1 and 4),[16] and alkanecarbaldehydes were mainly converted to 4-acetyl-5-alkyl-2(5*H*)-furanones **6** (Entries 6 and 7). In cases of $Ni(cod)_2/PPh_3$–Zn and $Pd(OAc)_2/PPh_3$–Zn, 5-substituted 4-acetyl-2(5*H*)-furanones **6** were produced from either of these aldehydes in high yields (Entries 2, 3, 5, and 8—11). The reaction on either of these catalytic systems: $Ni(cod)_2/PPh_3$–Zn and $Pd(OAc)_2/PPh_3$–Zn was faster than that on $PdCl_2(PhCN)_2$–$SnCl_2$ system. And ketones were also converted to **6** under the same conditions as those of aldehydes, in contrast with $PdCl_2(PhCN)_2$–$SnCl_2$ (Entries 12—15). The yield of **6** ($R^1=C_6H_5$, $R^2=H$) was 33% in the reaction using an amount of **4** equimolar to benzaldehyde with $Ni(cod)_2/PPh_3$–Zn at 60 °C for 24 h in dioxane. Using $PdCl_2(PhCN)_2$–$SnCl_2$ in acetonitrile, **5** ($R^1=C_6H_5$, $R^2=H$) was found to cause dehydrogenation with **4**, not at 50 °C but at 80 °C for 24 h to produce **6** ($R^1=C_6H_5$, $R^2=H$) in 75% yield. The pathway of the formation of **6** was thus investigated using *cis*-*β*-acetyl-*γ*-phenyl-*γ*-butyrolactones (**5**, $R=C_6H_5$) and *cis*-*β*-acetyl-*γ*-*t*-butyl-*γ*-butyrolactones (**5**, R=*t*-Bu) (Scheme 2).[17] Neither of these *γ*-butyrolactones caused any reaction without **4**, but with **4** the *γ*-butyrolactones caused dehydrogenation to convert to **6**, under the same conditions as those of the aldol-type reaction by **4** with $Ni(cod)_2/PPh_3$–Zn; **5** ($R=C_6H_5$, 1 mmol), **4** (2 mmol), Zn (2 mmol), 60 °C, 10 h, 79%; **5** (R=*t*-Bu, 1 mmol), **4** (2 mmol), Zn (2 mmol), 60 °C, 10 h, 69%.[18] *γ*-Methyl-*γ*-butyrolactone (0.67—0.80 mmol) was simultaneously produced. The dehydrogenation of **5** with **4** also occurred without zinc; 60 °C, 48 h, **6** ($R=C_6H_5$, 32%; R=*t*-Bu, 34%). $Pd(OAc)_2/PPh_3$ exhibited the same reactivity as that of $Ni(cod)_2/PPh_3$ in the dehydrogenaiton. These results suggest that **6** is produced via the aldol-type reaction of **4** and carbonyl compounds, followed by the dehydrogenation of **5** formed intermediately.

Experimental

General. Unless otherwise noted, all common reagents were used as obtained from commercial suppliers without further purification. All solvents were dried over desiccant and were distilled before being used. Bis(benzonitrile)dichloropalladium(II),[19] bis(triphenylphosphine)dibromonickel(II),[20] and bis(1,5-cyclooctadiene)nickel(0)[21] were prepared by the literature procedures. Methyl 10-oxodecanoate was prepared by the reaction of methyl 10-undecenoate with $OsO_4/NaIO_4$ at 25 °C in dioxane–H_2O.[22] 10-Oxoundecanal was prepared from 10-undecenal via Grignard reaction with methylmagnesium iodide, oxidation of alcohol

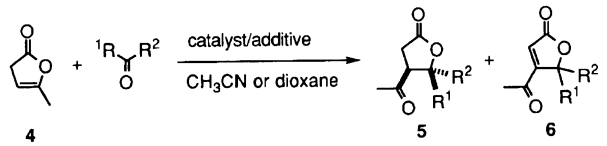


Scheme 1.



Scheme 2.

Table 4. Aldol-Type Condensation/Dehydrogenation of 5-Methyl-2(3*H*)-furanone (**4**)[a)]



4 **5** **6**

Entry	R^1	R^2	Catalyst/Additive	Time/h	Yield/%[b)]	
					5	**6**
1[c)]	C_6H_5	H	$PdCl_2(PhCN)_2/SnCl_2$	48	52[e)]	—
2[d)]	C_6H_5	H	$Ni(cod)_2$·$4PPh_3$/Zn	12	—	97
3[d)]	C_6H_5	H	$Pd(OAc)_2$·$2PPh_3$/Zn	12	—	93
4[c)]	$CH_3O_2CC_6H_4$	H	$PdCl_2(PhCN)_2/SnCl_2$	35	56[e)]	—
5[d)]	$(CH_3)_2CH$	H	$Ni(cod)_2$·$4PPh_3$/Zn	15	—	80
6[c)]	$(CH_3)_3C$	H	$PdCl_2(PhCN)_2/SnCl_2$	32	—	58
7[c)]	*n*-C_6H_{13}	H	$PdCl_2(PhCN)_2/SnCl_2$	32	8[e)]	20
8[d)]	*n*-C_6H_{13}	H	$Ni(cod)_2$·$4PPh_3$/Zn	14	—	78
9[d)]	*n*-C_6H_{13}	H	$Pd(OAc)_2$·$2PPh_3$/Zn	12	—	82
10[d)]	*c*-C_6H_{11}	H	$Ni(cod)_2$·$4PPh_3$/Zn	14	—	91
11[d)]	*c*-C_6H_{11}	H	$Pd(OAc)_2$·$2PPh_3$/Zn	12	—	80
12[d)]	CH_3CH_2	CH_3CH_2	$Ni(cod)_2$·$4PPh_3$/Zn	12	—	90
13[d)]	CH_3CH_2	CH_3CH_2	$Pd(OAc)_2$·$2PPh_3$/Zn	10	—	90
14[d)]	$(CH_2)_5$		$Ni(cod)_2$·$4PPh_3$/Zn	15	—	82
15[d)]	$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$		$Pd(OAc)_2$·$2PPh_3$/Zn	15	—	85

a) The reaction of **4** (2 mmol) and carbonyl compound (1 mmol) with catalyst (0.02 mmol) and additive (2 mmol) was carried out at 50—60 °C in acetonitrile or dioxane (5 ml) under an argon atmosphere. b) Isolated yields based on carbonyl compounds. c) The reaction was carried out at 50 °C in acetonitrile. d) The reaction was carried out at 60 °C in dioxane. e) >95% *cis*-Isomer (by 270 MHz ^{1}H NMR).

with pyridinium chlorochromate,[23)] followed by oxidative cleavage of alkene with $OsO_4/NaIO_4$.[22)] γ-Substituted β-acetyl-γ-butyrolactones were prepared by the reaciton of 5-methyl-2(3*H*)-furanone and aldehydes with *N*-chlorosuccinimide/$SnCl_2$.[17)] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 (270 MHz) spectrometer in $CDCl_3$. Infrared spectra were recorded on a JEOL JIR-RFX 3001 FTIR spectrometer. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX102 spectrometer. Purification of products was carried out by means of column chromatography (Merck Silica gel 60 Art.7734), preparative TLC (Harrison centrifugal thin-layer chromatotron; Merck silica gel 60 PF_{254} Art.7749), or HPLC (Japan Analytical Industry Co. Ltd. LC-908; JAIGEL-2H).

General Procedure of Palladium-Catalyzed Aldol-Type Condensation by Isopropenyl Acetate (1) with $SnCl_2$. To a solution of isopropenyl acetate (**1**, 0.31 g, 3 mmol), 4-methoxycarbonylbenzaldehyde (0.13 g, 1 mmol), and tin(II) chloride (0.57 g, 3 mmol) in acetonitrile (5 ml) was added bis(benzonitrile)dichloropalladium (8 mg, 0.02 mmol). This solution was stirred for 33 h at 50 °C under a nitrogen atmosphere. The reaction mixture was poured into water (30 ml) and extracted with ether–dichloromethane (4/1, 100 ml). The extract was washed first with water and then with brine, and was dried over $MgSO_4$. Evaporation of solvents and purification by preparative TLC (hexane : ethyl acetate=5 : 1) and/or HPLC afforded 0.18 g (88%, *E*: *Z*= 97 : 3) of 4-(4-methoxycarbonylphenyl)-3-buten-2-one (**3**; R= 4-$MeO_2CC_6H_4$) as a colorless solid.

General Procedure of Nickel- or Palladium-Catalyzed Aldol-Type Condensation by 1 with Zn. To a solution of isopropenyl acetate (**1**, 0.31 g, 3 mmol), benzaldehyde (0.11 g, 1 mmol), and zinc powder (0.20 g, 3 mmol) in dioxane (3 ml) were added bis(1,5-cyclooctadiene)nickel(0) (27 mg, 0.1 mmol) and PPh_3 (52 mg, 0.2 mmol). This solution was stirred for 48 h at 60 °C under an argon atmosphere. The reaction mixture was poured into water (30 ml) and extracted with ether-dichloromethane (4/1, 100 ml). The extract was washed first with water and then with brine, and was dried over $MgSO_4$. Evaporation of solvents and purification by preparative TLC (hexane : ethyl acetate=10 : 1) and/or HPLC afforded 99 mg (68%, *E*: *Z*=97 : 3) of 4-phenyl-3-buten-2-one (**3**; R=C_6H_5) as a colorless oil.

(*E*)-4-(4-Methoxycarbonylphenyl)-3-buten-2-one (Entries 2—9 in Table 1): ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s), 3.93 (3H, s), 6.78 (1H, d, *J*=16.3 Hz), 7.53 (1H, d, *J*=16.3 Hz), 7.60 (2H, d, *J*=8.5 Hz), and 8.06 (2H, d, *J*=8.5 Hz); IR (KBr) 2960, 1730, 1665, 1574, 1375, 1290, 1175, 1105, 980, and 760 cm^{-1}. Found: C, 70.69; H, 5.71%. Calcd for $C_{12}H_{12}O_3$: C, 70.56; H, 5.93%.

(*E*)-4-Phenyl-3-buten-2-one (Entry 10 in Table 1 and Entries 1—7 in Table 2):[24)] ^{1}H NMR ($CDCl_3$) δ=2.37 (3H, s), 6.71 (1H, d, *J*=16.2 Hz), 7.35—7.44 (3H, m), 7.51 (1H, d, *J*=16.2 Hz), and 7.50—7.58 (2H, m); IR (neat) 3050, 2950, 2920, 1660, 1620, 1450, 1250, 1018, 780, and 703 cm^{-1}.

(*E*)-4-(3,4-Methylenedioxyphenyl)-3-buten-2-one (Entry 11 in Table 1): ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, s), 5.97 (2H, s), 6.51 (1H, d, *J*=16.1 Hz), 6.77(1H, d, *J*=7.8 Hz), 6.98 (1H, d, *J*=7.8 Hz), 7.00 (1H, s), and 7.38 (1H, d, *J*=16.1 Hz); IR (KBr), 2960, 2840, 1640, 1600, 1360, 1240,

1115, 1040, 980, and 750 cm^{-1}. Found: C, 69.72; H, 5.11%. Calcd for $C_{11}H_{10}O_3$: C, 69.45; H, 5.30%.

(*E*)-4-(2-Methoxyphenyl)-3-buten-2-one (Entry 12 in Table 1 and Entries 8—12 in Table 2): ^1H NMR ($CDCl_3$) δ=2.38 (3H, s), 3.89 (3H, s), 6.75 (1H, d, J=16.6 Hz), 6.92 (1H, d, J=7.8 Hz), 6.96 (1H, t, J=7.8 Hz), 7.36 (1H, t, J=7.8 Hz), 7.54 (1H, d, J=7.8 Hz), and 7.88 (1H, d, J=16.6 Hz); IR (neat) 3050, 3000, 2960, 2930, 2840, 1662, 1598, 1358, 1240, 1175, 1105, 980, and 750 cm^{-1}; MS m/z (rel intensity) 176 (38), 161 (92), 146 (26), 145 (100), 118 (24), 105 (25), and 77 (16). HRMS Found: m/z 176.0835. Calcd for $C_{11}H_{12}O_2$: M, 176.0837.

(*E*)-4-(4-Nitrophenyl)-3-buten-2-one (Entry 13 in Table 1): ^1H NMR ($CDCl_3$) δ=2.44 (3H, s), 6.84 (1H, d, J=15.9 Hz), 7.57 (1H, d, J=15.9 Hz), 7.73 (2H, d, J=9.2 Hz), and 8.26 (2H, d, J=9.2 Hz); IR (KBr) 3064, 1670, 1596, 1574, 1349, 1211, 1110, 984, and 746 cm^{-1}; MS m/z (rel intensity) 191 (M^+, 76), 177 (23), 176 (100), 174 (79), 144 (19), 130 (53), 118 (16), 102 (46), 90 (17), and 76 (16). HRMS Found: m/z 191.0580. Calcd for $C_{10}H_9NO_3$: M, 191.0582.

(*E*)-4-(4-Cyanophenyl)-3-buten-2-one (Entry 14 in Table 1): ^1H NMR ($CDCl_3$) δ=2.41 (3H, s), 6.78 (1H, d, J=16.5 Hz), 7.50 (1H, d, J=16.5 Hz), 7.64 (2H, d, J=8.5 Hz), 7.70 (2H, d, J=8.5 Hz); IR (KBr) 2924, 2227, 1677, 1506, 1366, 1175, 1105, 980, and 760 cm^{-1}; Found: C, 77.33; H, 5.21; N, 7.98%. Calcd for $C_{11}H_9NO$: C, 77.16; H, 5.30; N, 8.19%.

(*E*)-4-(4-Chlorophenyl)-3-buten-2-one (Entry 15 in Table 1): ^1H NMR ($CDCl_3$) δ=2.38 (3H, s), 6.68 (1H, d, J=16.5 Hz), 7.35—7.49 (5H, m); IR (KBr) 2970, 1660, 1506, 1366, 1175, 1105, 980, 760, and 489 cm^{-1}; MS m/z (rel intensity) 182 (15), 181 (9), 180 (46), 179 (15), 167 (34), 165 (100), 145 (20), 137 (30), 102 (19), and 101 (21). HRMS Found: m/z 180.0336. Calcd for $C_{10}H_9O^{35}Cl$: M, 180.0342. HRMS Found: m/z 182.0309. Calcd for $C_{10}H_9O^{37}Cl$: M, 182.0313.

1,3-Bis(3-oxo-1-butenyl)benzene (Entry 16 in Table 1): ^1H NMR ($CDCl_3$) δ=2.40 (6H, s), 6.75 (2H, d, J=16.5 Hz), 7.42—7.59 (3H, m), 7.52 (2H, d, J=16.5 Hz), and 7.69 (1H, s); IR (KBr) 2999, 1673, 1600, 1360, 1163, 985, and 784 cm^{-1}; MS m/z (rel intensity) 214 (M^+, 100), 213 (24), 199 (48), 171 (85), 157 (40), and 128 (19). HRMS Found: m/z 214.0997. Calcd for $C_{14}H_{14}O_2$: M, 214.0993.

(3*E*,5*E*)-6-Phenyl-3,5-hexadien-2-one (Entry 17 in Table 1):[5] ^1H NMR ($CDCl_3$) δ=2.32 (3H, s), 6.27 (1H, d, J=15.3 Hz), 6.88 (1H, dd, J=15.6, 9.5 Hz), 6.97 (1H, d, J=15.6 Hz), and 7.25—7.52 (6H, m); IR (neat) 3050, 2940, 1735, 1368, 1230, 1110, 991, 750, and 695 cm^{-1}.

(*E*)-6-Phenyl-3-hexen-2-one (Entry 18 in Table 1 and Entries 16—18 in Table 2): ^1H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.55 (2H, br.q, J=6.8 Hz), 2.79 (2H, br.t, J=7.4 Hz), 6.09 (1H, d, J=16.1 Hz), and 6.82 (1H, dt, J=16.1, 6.8 Hz), and 7.14—7.36 (5H, m); IR (neat) 3027, 2925, 1697, 1675, 1626, 1454, 1360, 1254, 975, 748, and 700 cm^{-1}; MS m/z (rel intensity) 174 (M^+, 5), 149 (23), 116 (14), 105 (14), 97 (12), 92 (13), 91 (100), 83 (8), 77 (11), 71 (11), and 69 (9). HRMS Found: m/z 174.1046. Calcd for $C_{12}H_{14}O$: M, 174.1044.

(*E*)-3,13-Tetradecadien-2-one (Entry 19 in Table 1 and Entries 19—23 in Table 2): ^1H NMR ($CDCl_3$) δ= 1.20—1.53 (12H, br), 1.98—2.10 (2H, m), 2.15—2.28 (2H, m), 2.24 (3H, s), 4.93 (1H, d, J=10.2 Hz), 5.00 (1H, d, J=16.9 Hz), 5.81 (1H, ddt, J=16.9, 10.2, 6.6 Hz), and 6.07 (1H, d, J=15.8 Hz), and 6.80 (1H, dt, J=15.8, 6.8 Hz); IR (neat) 3074, 3027, 2927, 2854, 1698, 1677, 1640, 1628, 1360, 1439, 1360, 1253, 978, and 910 cm^{-1}; MS m/z (rel intensity) 208 (M^+, 18), 150 (26), 149 (62), 111 (24), 109 (34), 97 (100), 96 (25), 95 (58), 85 (22), 84 (40), 83 (38), 82 (29), 81 (57), 79 (20), 71 (67), 69 (52), 68 (25), 67 (44), 57 (44), and 55 (91). HRMS Found: m/z 208.1820. Calcd for $C_{14}H_{24}O$: M, 208.1826.

(3*Z*,5*E*)-6-Phenyl-3,5-hexadien-2-one (Entries 13—15 in Table 2): ^1H NMR ($CDCl_3$) δ=2.11 (3H, d, J=3.4 Hz), 5.66 (1H, d, J=6.8 Hz), 6.06—6.22 (1H, m), 6.71 (1H, d, J=15.6 Hz), and 7.21—7.41 (6H, m); IR (neat) 3075, 3050, 3025, 2940, 1740, 1370, 1230, 1110, 982, 750, and 695 cm^{-1}; MS m/z (rel intensity) 175 (84), 149 (31), 134 (22), 133 (100), 115 (22), 91 (11), 85 (12), 83 (10), 71 (20), 69 (21), 57 (30), and 55 (17). Found: C, 83.56; H, 6.83%. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03%.

(*E*)-6,10-Dimethyl-3,9-undecadien-2-one (Entries 24—26 in Table 2): ^1H NMR ($CDCl_3$) δ=0.92 (3H, d, J=6.8 Hz), 1.12—1.43 (2H, m), 1.60 (3H, s), 1.64 (1H, br), 1.69 (3H, s), 1.91—2.14 (4H, m), 2.25 (3H, s), 5.08 (1H, t, J=6.8 Hz), 6.07 (1H, d, J=15.8 Hz), and 6.78 (1H, dt, J=15.8, 7.3 Hz); IR (neat) 3030, 2960, 2920, 2880, 1678, 1625, 1455, 1360, 1250, and 980 cm^{-1}; MS m/z (rel intensity) 194 (M^+, 180), 179 (23), 167 (55), 151 (22), 149 (100), 137 (50), 136 (49), 123 (29), 121 (21), 111 (26), 109 (61), 95 (50), 93 (22), 83 (23), 82 (25), 81 (39), 71 (24), 70 (21), 69 (94), 57 (32), and 55 (43). HRMS Found: m/z 194.1681. Calcd for $C_{13}H_{22}O$: M, 194.1670.

(*E*)-4-(3-Cyclohexenyl)-3-buten-2-one (Entries 27 and 28 in Table 2): ^1H NMR ($CDCl_3$) δ=1.40—1.59 (1H, m), 1.73—2.27 (5H, m), 2.26 (3H, s), 2.39—2.53 (1H, m), 5.64—5.77 (2H, m), 6.08 (1H, dd, J=16.1,1.5 Hz), and 6.80 (1H, dd, J=16.1, 7.1 Hz); IR (neat) 3023, 2915, 2837, 1699, 1676, 1626, 1436, 1364, 1253, 981, and 658 cm^{-1}; MS m/z (rel intensity) 150 (M^+, 16), 107 (43), 96 (16), 95 (25), 93 (20), 92 (59), 91 (36), 81 (100), 80 (39), 79 (72), 77 (25), 67 (19), and 55 (39). HRMS Found: m/z 150.1056. Calcd for $C_{10}H_{14}O$: M, 150.1056.

Methyl (*E*)-12-Oxo-10-tridecenoate (Entry 29 in Table 2): ^1H NMR ($CDCl_3$) δ=1.26—1.36 (8H, br), 1.57—1.67 (4H, br), 2.07 (3H, s), 2.19—2.34 (4H, m), 3.67 (3H, s), 6.07 (1H, d, J=15.8 Hz), and 6.80 (1H, dt, J=15.8, 6.5 Hz); IR (neat) 2930, 2857, 1740, 1701, 1676, 1636, 1617, 1437, 1369, 1251, 1208, 1107, 1011, and 977 cm^{-1}; MS m/z (rel intensity) 240 (M^+, 24), 209 (55), 208 (38), 201 (71), 199 (54), 182 (23), 169 (100), 165 (34), 157 (63), 151 (23), 150 (81), 144 (21), 125 (38), 124 (23), 123 (39), 122 (25), 109 (23), 108 (26), 98 (52), 97 (70), 96 (22), 95 (31), 87 (53), 84 (52), 83 (32), 81 (65), 74 (75), 71 (35), 69 (45), 67 (38), 59 (24), and 55 (82). HRMS Found: m/z 240.1730. Calcd for $C_{14}H_{24}O_3$: M, 240.1724.

(*E*)-3-Tetradecene-2,13-dione (Entry 30 in Table 2): ^1H NMR ($CDCl_3$) δ=1.22—1.36 (8H, br), 1.41—1.63 (4H, m), 2.13 (3H, s), 2.17—2.27 (2H, m), 2.24 (3H, s), 2.42 (2H, t, J=7.2 Hz), and 6.07 (1H, br d, J=15.7Hz), and 6.80 (1H, dt, J=15.7, 7.0 Hz); IR (neat) 3002, 2929, 2854, 1718, 1676, 1628, 1362, 1254, and 981 cm^{-1}; MS m/z (rel intensity) 224 (M^+, 29), 167 (32), 149 (100), 123 (30), 111 (24), 109 (37), 108 (23), 97 (86), 95 (31), 85 (27), 84 (31), 83 (37),

81 (49), 71 (70), 69 (62), 67 (24), 58 (29), 57 (58), and 55 (56). HRMS Found: m/z 224.1774. Calcd for $C_{14}H_{24}O_2$: M, 224.1775.

General Procedure of Palladium-Catalyzed Aldol-Type Condensation by 5-Methyl-2(3*H*)-furanone (4) with $SnCl_2$. To a solution of 5-methyl-2(3*H*)-furanone (**4**, 0.20 g, 2 mmol), benzaldehyde (0.11 g, 1 mmol), and tin(II) chloride (0.38 g, 2 mmol) in acetonitrile (5 ml) was added bis(benzonitrile)dichloropalladium (8 mg, 0.02 mmol). This solution was stirred for 48 h at 50 °C under a nitrogen atmosphere. The reaction mixture was poured into water (30 ml) and extracted with ether–dichloromethane (4/1, 100 ml). The extract was washed first with water and then with brine, and was dried over $MgSO_4$. Evaporation of solvents and purification by preparative TLC (hexane : ethyl acetate=3 : 1) afforded 0.11 g (52%) of β-acetyl-γ-phenyl-γ-butyrolactone as a colorless oil.

β-Acetyl-γ-phenyl-γ-butyrolactone (Entry 1 in Table 4): ^{1}H NMR ($CDCl_3$) δ=2.07 (3H, s), 2.83 (2H, d, J=9.4 Hz), 3.53 (1H, q, J=9.4 Hz), 5.51 (1H, d, J=7.9 Hz), and 7.33 (5H, s); IR (neat) 3066, 2929, 1773, 1717, 1270, 1174, 1016, 956, and 765 cm^{-1}; MS m/z (rel intensity) 204 (M^+, 50), 176 (22), 162 (92), 161 (100), 147 (66), 133 (26), 115 (21), 105 (59), 98 (43), 77 (28), 71 (26), 70 (20), 57 (36), and 55 (47). HRMS Found: m/z 204.0787. Calcd for $C_{12}H_{12}O_3$: M, 204.0786.

β-Acetyl-γ-(4-methoxycarbonylphenyl)-γ-butyrolactone (Entry 4 in Table 4): ^{1}H NMR ($CDCl_3$) δ=2.20 (3H, s), 2.88 (1H, dd, J=17.4, 9.4 Hz), 2.94 (1H, dd, J=17.4, 9.4 Hz), 3.51 (1H, q, J=9.4 Hz), 3.95 (3H, s), 5.57 (1H, d, J=9.4 Hz), 7.43 (2H, d, J=8.1 Hz), and 8.06 (2H, d, J=8.1 Hz); IR (neat) 3066, 2997, 1773, 1718, 1276, 1114, 1028, and 951 cm^{-1}. HRMS Found: m/z 262.0840. Calcd for $C_{14}H_{14}O_5$: M, 262.0840.

β-Acetyl-γ-hexyl-γ-butyrolactone (Entry 7 in Table 4): ^{1}H NMR ($CDCl_3$) δ=0.86—0.97 (3H, br), 1.23—1.52 (8H, br), 1.65—1.72 (2H, m), 2.26 (3H, s), 2.69—2.86 (2H, m), 3.18 (1H, dt, J=8.3, 6.8 Hz), and 4.59 (1H, dt, J=6.8, 5.9 Hz), IR (neat) 2930, 1781, 1718, 1363, 1200, 1001, and 949 cm^{-1}; MS m/z (rel intensity) 212 (M^+, 14), 170 (46), 127 (100), 114 (30), 113 (31), 100 (94), 99 (26), 98 (33), 85 (58), 71 (37), and 55 (46). HRMS Found: m/z 212.1409. Calcd for $C_{12}H_{20}O_3$: M, 212.1411.

General Procedure of Nickel-Catalyzed Aldol-Type Condensation/Dehydrogenation by 4 with Zn. To a solution of 5-methyl-2(3*H*)-furanone (**4**, 0.20 g, 2 mmol), benzaldehyde (0.11 g, 1 mmol), and zinc powder (0.13 g, 2 mmol) in dioxane (5 ml) were added bis(1,5-cyclooctadiene)nickel(0) (6 mg, 0.02 mmol) and PPh_3 (21 mg, 0.08 mmol). This solution was stirred for 12 h at 60 °C under an argon atmosphere. The reaction mixture was poured into water (30 ml) and extracted with ether–dichloromethane (4/1, 100 ml). The extract was washed first with water and then with brine, and was dried over $MgSO_4$. Evaporation of solvents and purification by preparative TLC (hexane : ethyl acetate=5 : 1) afforded 0.20 g, (97%) of 4-acetyl-5-phenyl-2(5*H*)-furanone as a colorless oil.

4-Acetyl-5-phenyl-2(5*H*)-furanone (Entries 2 and 3 in Table 4): ^{1}H NMR ($CDCl_3$) δ=2.18 (3H, s), 6.28 (1H, s), 7.26 (1H, s), 7.35—7.45 (3H, m), and 7.49—7.56 (2H, m); ^{13}C NMR ($CDCl_3$) δ=14.7, 102.0, 125.5, 128.9, 129.8, 129.9, 133.8, 135.1, 158.3, and 169.8; IR (neat) 3056, 2917, 1776, 1637, 1282, 1160, 1029, 927, 763, and 692 cm^{-1}; MS m/z (rel intensity) 202 (M^+, 30), 187 (36), 186 (100), 167 (26), 159 (25), 158 (59), 149 (66), 116 (48), 115 (93), 105 (58), and 77 (28). HRMS Found: m/z 202.0625. Calcd for $C_{12}H_{10}O_3$: M, 202.0629.

4-Acetyl-5-isopropyl-2(5*H*)-furanone (Entry 5 in Table 4): ^{1}H NMR ($CDCl_3$) δ=1.10 (6H, d, J=6.7 Hz), 2.11 (3H, s), 2.65 (1H, dseptet, J=9.7, 6.7 Hz), 5.83 (1H, s), 6.41 (1H, d, J=9.7 Hz); ^{13}C NMR ($CDCl_3$) δ=14.5, 22.0, 30.0, 100.7, 126.1, 145.7, 155.7, and 169.0; IR (neat) 3116, 2963, 1783, 1388, 1130, 1028, 923, and 741 cm^{-1}; MS m/z (rel intensity) 168 (M^+, 41), 167 (36), 166 (82), 153 (29), 152 (29), 151 (25), 143 (35), 126 (100), 125 (84), 124 (99), 123 (28), 98 (47), 97 (41), 96 (27), 71 (56), 69 (24), and 55 (23). HRMS Found: m/z 168.0783. Calcd for $C_9H_{12}O_3$: M, 168.0786.

4-Acetyl-5-*t*-butyl-2(5*H*)-furanone (Entry 6 in Table 4): ^{1}H NMR ($CDCl_3$) δ=1.20 (9H, s), 2.11 (3H, s), 5.98 (1H, s), and 6.57 (1H, s); IR (neat) 2965, 2908, 1778, 1653, 1447, 1294, 1138, 999, and 922 cm^{-1}; MS m/z (rel intensity) 182 (M^+, 16), 142 (38), 139 (32), 126 (45), 125 (33), 124 (92), 98 (35), 97 (21) and 57 (100). HRMS Found: m/z 182.0930. Calcd for $C_{10}H_{14}O_3$: M, 182.0942.

4-Acetyl-5-hexyl-2(5*H*)-furanone (Entry 7—9 in Table 4): ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=6.8 Hz), 1.22—1.40 (6H, m), 1.43—1.56 (2H, m), 2.11 (3H, s), 2.29 (2H, q, J=7.5 Hz), 5.81 (1H, br), and 6.56 (1H, t, J=7.5 Hz); IR (neat) 2956, 2927, 2857, 1781, 1652, 1456, 1271, 1159, 981, 922, and 738 cm^{-1}; MS m/z (rel intensity) 210 (M^+, 12), 209 (31), 181 (20), 139 (34), 125 (24), 114 (28), 113 (100), 97 (39), 85 (30), 71 (24), 57 (20), and 55 (30). HRMS Found: m/z 210.1251. Calcd for $C_{12}H_{18}O_3$: M, 210.1255.

4-Acetyl-5-cyclohexyl-2(5*H*)-furanone (Entries 10 and 11 in Table 4): ^{1}H NMR ($CDCl_3$) δ=1.08—1.37 (5H, m), 1.55—1.78 (5H, m), 2.06 (3H, s), 2.20—2.39 (1H, m), 5.78 (1H, s), and 6.37 (1H, d, J=9.8 Hz). IR (neat) 2926, 2853, 1779, 1649, 1449, 1269, 1024, 921, and 739 cm^{-1}; MS m/z (rel intensity) 208 (M^+, 13), 206 (29), 192 (21), 163 (21), 126 (34), 124 (51), 98 (57), 83 (100), and 55 (77). HRMS Found: m/z 208.1101. Calcd for $C_{12}H_{16}O_3$: M, 208.1099.

4-Acetyl-5,5-diethyl-2(5*H*)-furanone (Entries 12 and 13 in Table 4): ^{1}H NMR ($CDCl_3$) δ=1.10 (3H, t, J=7.4 Hz) 1.11 (3H, t, J=7.4 Hz), 2.08 (3H, s), 2.32 (2H, q, J=7.4 Hz), and 2.79 (2H, q, J=7.4 Hz), and 5.79 (1H, s); IR (neat) 2972, 2936, 1765, 1651, 1463, 1278, 1046, 932, and 758 cm^{-1}; MS m/z (rel intensity) 182 (M^+, 18), 179 (29), 167 (27), 166 (100), 165 (23), 153 (25), 137 (31), 124 (34), 123 (21), 110 (32), and 57 (20). HRMS Found: m/z 182.0942. Calcd for $C_{10}H_{14}O_3$: M, 182.0942.

3′-Acetylspiro[cyclohexane-1,2′(5*H*′)-furan]-5′-one (Entry 14 in Table 4): ^{1}H NMR ($CDCl_3$) δ=1.57—1.80 (6H, br), 2.08 (3H, s), 2.30—2.45 (2H, br), 2.94—3.10 (2H, br), and 5.79 (1H, br); IR (neat) 2935, 2857, 1761, 1652, 1449, 1276, 1049, 933, and 756 cm^{-1}; MS m/z (rel intensity) 194 (M^+, 35), 178 (100), 167 (24), 165 (20), 151 (20), 149 (65), 124 (24), 111 (41), 110 (52), 71 (21), 57 (22), and 55 (29). HRMS Found: m/z 194.0948. Calcd for $C_{11}H_{14}O_3$: M, 194.0942.

3′-Acetyl-4-*t*-butylspiro[cyclohexane-1,2′(5*H*′)-furan]-5′-one (Entry 15 in Table 4): ^{1}H NMR ($CDCl_3$) δ=0.86 (9H, s), 1.08—1.38 (3H, m), 1.85—2.19 (4H, m),

2.07 (3H, s), 2.61—2.69 (1H, m), 4.09—4.18 (1H, m), and 5.80 (1H, s); IR (KBr) 2955, 2867, 1778, 1653, 1447, 1294, 1067, 999, and 786 cm^{-1}; MS m/z (rel intensity) 250 (M^+, 80), 235 (34), 234 (100), 233 (42), 207 (41), 195 (36), 193 (46), 165 (54), 155 (33), 152 (30), 149 (63), 57 (100), and 55 (40). HRMS Found: m/z 250.1572. Calcd for $C_{15}H_{22}O_3$: M, 250.1568.

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