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Mild and Practical Acylation of Alcohols with Esters or Acetic Anhydride under Distannoxane Catalysis

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Abstract: Distannoxane catalysts effect acylation of alcohols by action of esters and acetic anhydride. In particular, use of enol esters provides an extremely useful method. Primary alcohols are acylated in preference to secondary ones as well as phenol. Both acid- and base-sensitive functional groups remain intact. Especially unique is the discrimination of thio function which is completely tolerant under the present reaction conditions. This method is highly practical since operation is quite simple. Esters and solvents can be used without purification and no inert atmosphere is necessary. The products can be isolated simply by column chromatography or distillation without aqueous workup.

INTRODUCTION

Acylation of alcohols is one of the most important manipulations in organic synthesis and a number of reagents coupled with promoters or catalysts have been put forth. Among them, acid anhydrides are the most frequently employed reagents. Probably, the first practical breakthrough in this technology was brought about by the discovery of the 4-dialkylaminopyridine catalysts.[1] This protocol has been undergoing further improvements.[2] In addition, a variety of new catalysts appeared which are either basic or acidic. For example, tertiary phosphines[3] and an aminophosphine superbase[4] fall in the former category while *p*-toluenesulfonic acid,[5] $ZnCl_2$,[6] $CoCl_2$,[7] $Sc(OTf)_3$,[8] TMSOTf,[9] $TaCl_5$-SiO_2,[10] Montmorillonite,[11] and zeolite[12] in the latter. A dual $MgBr_2$/tertiary amine array[13] and the reaction at high temperatures (95-105 °C) without catalyst[14] were also reported.

Transesterification[15] by use of esters as acylating reagents is another important and versatile means[16] but, unfortunately, this reaction is difficult to reach high conversion due to its reversibility. This drawback can be overcome by using enol esters which are capable of escaping from the equilibrium because of their conversion into aldehydes or ketones upon transesterification. The reaction is usually conducted under acidic conditions.[17] Recently, $Cp^*_2Sm(thf)_2$ or SmI_2 was found to be effective, yet this method required the Schlenk tube technique.[18] It follows that further improvements are needed in order for this protocol to find broader uses in the practical sense.

Acid chlorides,[19] acetic acid[16i,20] and methyl orthoacetate[21] served as well. In addition to these classical ones, a variety of new acylating reagents were also developed.[22] Despite these modifications, the two

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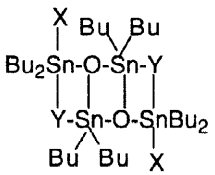
protocols which employ acid anhydrides or esters are most promising in terms of facile manipulations and availability of the reagents.

1,3-Disubstituted tetraalkyldistannoxanes with a dimeric formulation **1** are Lewis acids that are able to catalyze various carbonyl transformations under virtually neutral conditions.[23] These precedents have led us to explore new methods for acylation of alcohols under mild conditions. Herein is described that the distannoxane catalysts effect practical acylation reactions on the basis of the transesterification and acid anhydride protocols.[24]



1a: X = Y = Cl; **1b**: X = Y = -NCS
1c: X = Cl, Y = OH; **1d**: X = -NCS, Y = OH

RESULTS AND DISCUSSION

This study has its foundation on our previous findings that distannoxanes smoothly catalyze transesterification.[25] Thus, we first addressed ourselves to investigate acetylation of phenylethanols by use of ethyl acetate (Table 1). 2-Phenylethanol (**2a**) in EtOAc was heated under reflux for 12 h in the presence of **1a**. With 10 and 5 mol % catalyst concentrations, the desired ester was obtained quantitatively (entries 1 and 2) whereas the use of 1 mol % catalyst slightly decreased the yield (entry 3). With this catalyst concentration, the yield dropped sharply at lower temperatures (entries 4 and 5). 1-Phenylethanol (**2b**) is less reactive but the refluxing conditions with 10 mol % catalyst gave an 82% yield (entry 6). Transesterification-based acylations were reported with organotin alkoxides,[16a] alumina,[16b,c] $Ti(OR)_4$,[16d,e] metallic sulfates,[16f,g] lanthanoid triisopropoxides[16h] and butylstannoic acid.[16i] All these reactions required heating at 50~110 °C. In this context, the catalytic activity of distannoxane is not so significantly different from those of the so far reported catalysts or promoters.

Table 1. Distannoxane-Catalyzed Acetylation with Ethyl Acetate.[a]

ROH + EtOAc $\xrightarrow{\mathbf{1}}$ ROAc

Entry	Alcohol	**1** (mol %)[b]	Condns (°C, h)	ester (% yield)[c]
1	$Ph(CH_2)_2OH$ (**2a**)	**1a**, 10	reflux, 12	98
2	**2a**	**1a**, 5	reflux, 12	96
3	**2a**	**1a**, 1	reflux, 12	91
4	**2a**	**1a**, 1	50, 24	52
5	**2a**	**1a**, 1	30, 24	17
6	$PhCH(OH)CH_3$ (**2b**)	**1a**, 10	reflux, 12	82

[a] Reaction conditions: alcohol (5 mmol); EtOAc (10 mL). [b] Molarity on the basis of the monomeric formulation. [c] Isolated yield after column chromatography.

Although the above transesterification protocol seemed to be substantially useful, we were intrigued by the enol ester variant with a view towards further enhancement of the reactivity (eq. 1). The operation is quite simple. A solution of **2** (5 mmol) and a catalytic amount of distannoxane **1** in enol ester **3** (5 mL) was stirred under conditions given in Table 2. The reaction mixture was evaporated and the residue was subjected to column chromatography to give the desired esters **4**. First, variations of the distannoxane catalysts were examined (entries 1-4). No significant difference in the catalytic activity was observed between 1,3-dichloro and -diisothiocyanato derivatives, **1a** and **1b**, and both are more active than the corresponding monohydroxy derivatives, **1c** and **1d**. As a consequence, **1a** that can be obtained most conveniently was the catalyst of our choice in this study. The reaction proceeded quantitatively at 30 °C even with 1 mol % catalyst though the reaction rate decreased with decreasing catalyst concentration (entries 5-7). The reaction time can be shortened by elevating the reaction temperature (entries 8 and 9). When the substrate is insoluble in enol esters, a co-solvent like toluene or THF may be used (entries 10 and 11). 1-Octanol (**2c**) reacted similarly (entries 12 and 13). Isopropenyl acetate (**3b**), vinyl benzoate (**3c**), acrylate (**3d**), pivalate (**3e**), and chloroacetate (**3f**) also served as acylating reagents to afford the desired esters quantitatively (entries 14-19). The reaction of secondary alcohols was controlled simply by changing the reaction temperature: the reaction was sluggish at 30 °C (entries 20 and 22) but proceeded quantitatively at refluxing temperature in **3a** (72 °C) (entries 21 and 23). Benzyl alcohol (**2e**) was also employable but its reactivity was somewhat lower than that of aliphatic alcohols (entries 24 and 25). Cyclohexanol failed to react at 30 °C (entry 26) and, more remarkably, phenol that is more reactive than aliphatic alcohols under basic conditions did not undergo acetylation (entry 27). It is added to note that the use of only 1.3 equiv. of **3a**, when it is desirable, furnished **4a** in 97% yield in the reation of **2a** in the presence of 5 mol % of **1a** at 30 °C.

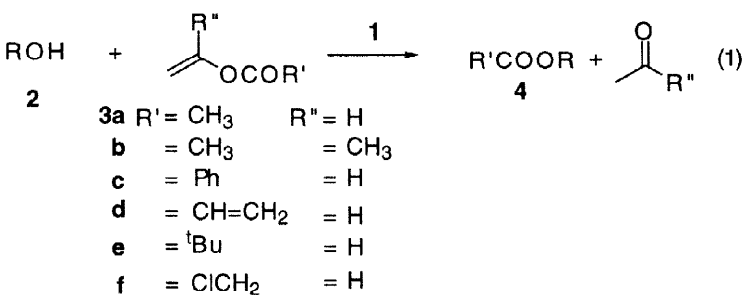


Table 2. Acylation with Alkenyl Esters[a)]

Entry	2	1 (mol %)[b)]	3a	Condns (°C, h)	4 (% yield)[c)]
1	**2a**	**1a**, 5	**3a**	30, 5	93
2	**2a**	**1b**, 5	**3a**	30, 5	99
3	**2a**	**1c**, 5	**3a**	30, 5	36
4	**2a**	**1d**, 5	**3a**	30, 5	40
5	**2a**	**1a**, 3	**3a**	30, 8	99
6	**2a**	**1a**, 2	**3a**	30, 11	98
7	**2a**	**1a**, 1	**3a**	30, 21	98
8	**2a**	**1a**, 1	**3a**	50, 2.5	98
9	**2a**	**1a**, 1	**3a**	reflux, <0.5	99

(Table 2 continued)

10	**2a**	**1a**, 5	**3a**	30, 13[d]	98
11	**2a**	**1a**, 5	**3a**	30, 13[e]	98
12	*n*-$C_8H_{17}OH$ (**2c**)	**1a**, 3	**3a**	30, 8	97
13	**2c**	**1a**, 1	**3a**	30, 20	98
14	**2a**	**1a**, 5	**3b**	30, 24	98
15	**2a**	**1a**, 1	**3b**	reflux, 2	99
16	**2c**	**1a**, 5	**3c**[f]	50, 15	98[g]
17	**2c**	**1a**, 5	**3d**[f]	50, 15	98
18	**2c**	**1a**, 5	**3e**[f]	50, 15	97
19	**2c**	**1a**, 5	**3f**[f]	50, 17	96
20	**2b**	**1a**, 10	**3a**	30, 24	2
21	**2b**	**1a**, 10	**3a**	reflux, 0.5	99
22	$C_6H_{13}CH(OH)CH_3$ (**2d**)	**1a**, 1	**3a**	30, 24	11
23	**2d**	**1a**, 10	**3a**	reflux, 1	97
24	$PhCH_2OH$ (**2e**)	**1a**, 3	**3a**[f]	30, 14	98
25	**2e**	**1a**, 5	**3b**[f]	30, 42	91[h]
26	cyclohexanol	**1a**, 1	**3a**	30, 24	0
27	C_6H_5OH	**1a**, 10	**3a**	30, 24	trace

[a] Reaction conditions: **2** (5 mmol), **3** (5 mL). [b] Molarity on the basis of the monomeric formulation. [c] Isolated yield after column chromatography. [d] In **3a** (2.5 mL) and toluene (2.5 mL). [e] In **3a** (2.5 mL) and THF (2.5 mL). [f] **3** (3 mL). [g] Determined by ^1H NMR. [h] TLC monitoring indicated a small amount of **2e** remaining.

The above results led us to postulate the discrimination of primary alcohols from secondary ones. In general, the high level of discrimination at high conversion is difficult to attain because acylation of the less reactive secondary alcohol component is accelerated at the later stage of the reaction, leading to the alternative of modest yield with high selectivity or poor selectivity with high yield. Most of foregoing studies failed to overcome this paradoxical difficulty, resulting in less than 70% yields or the selectivity not exceeding 90%.[16a,e,f,i,22c,d,g] To the best of our knowledge, only the following precedent examples satisfied the above demands: 3-acyl-2-oxazolone/Zr complex,[22e] 1-(benzoyloxy)benzotriazole,[22f] 3-acetylthiazolidine-2-thiones,[22h,i] acetyl chloride/hindered amine[19c] and methyl orthoacetate/rare earth metal salts.[21] The distannoxane method provides a more convenient access to this issue. As shown in Scheme 1, competition reactions between these two classes of alcohols at 30 °C resulted in selective or exclusive formation of primary acetates when isopropenyl acetate (**3b**) was employed. With more reactive vinyl acetate (**3a**), the differentiation was induced satisfactorily between the phenylethanols but poorly between the octanols.

Scheme 1.[a,b]

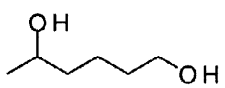
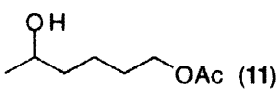
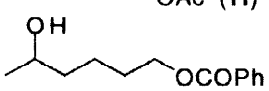
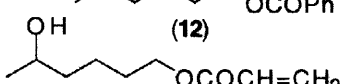
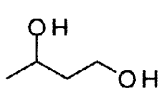
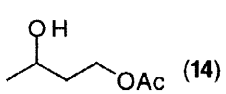
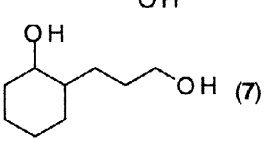
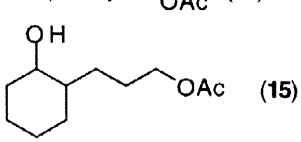
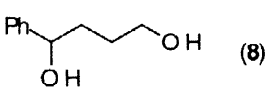
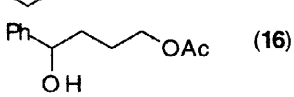
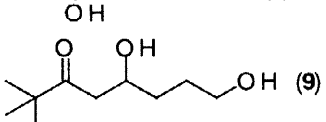
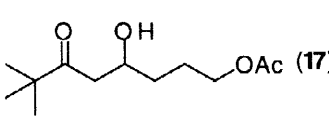
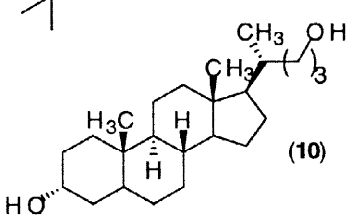
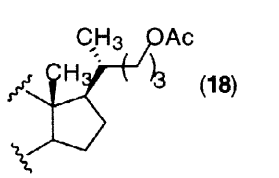
$$ROH + R'CH(OH)CH_3 \xrightarrow{\textbf{1a/3}} ROAc + R'CH(OAc)CH_3$$

2a	**2b**	[**1a** (1 mol %); **3a**]	99%	1%
2a	**2b**	[**1a** [5 mol %); **3b**]	99%	0%
2c	**2d**	[**1a** (1 mol %); **3a**]	99%	18%
2c	**2d**	[**1a** (3 mol %); **3b**]	99%	2%

[a] Reaction conditions: alcohols (5 mmol each); **3** (5 mL); 30 °C; 24 h.
[b] Yields determined by GLC.

The unique but versatile selectivities are highlighted by intramolecular versions in Table 3 where results from some representative acidic and basic methods are also given for comparison. With 1,5-hexanediol (**5**), the distannoxane method exhibited the high preference for the primary hydroxyl over the secondary one to afford the desired mono esters (entries 1-3) whereas the diacetate was a sole product by the other methods (entries 4-6). 1,3-Butanediol reacted similarly (entry 7). Cyclohexanol and secondary benzylic alcohol suffered more reduced reactivity to provide the perfect bias in favor of the primary alcohol (entries 8 and 9). An aldol product **9** underwent smooth acetylation on the primary hydroxyl without dehydration (entry 10). The selective acetylation is also applicable to a steroid derivative **10**. It should be noted, however, that when 1,2-octanediol was subjected to the same reaction conditions (40 °C; 50 h), the monoacetates (in 72:28 ratio of primary and secondary acetates) and the diacetate were obtained in 31 and 24% yields, respectively.

Table 3. Selective Acylation of the Primary Hydroxyl in Diols

Entry	Diol	Reactn Conditn	Monoester (% yield)		% Yield of Diester
1	 (**5**)	**5** (3 mmol);**1a** (2 mol %); **3b** (5 mL); 30 °C; 24 h	 (**11**)	92	1
2	**5**	**5** (5 mmol);**1a** (10 mol %); **3c** (3 mL); 50 °C; 40 h	 (**12**)	96	1
3	**5**	**5** (5 mmol);**1a** (10 mol %); **3d** (3 mL); 30 °C; 45 h	 (**13**)	96	0
4	**5**	**5** (5 mmol); $Sc(OTf)_3$ (1 mol %); Ac_2O (3 mL); 30 °C, 24 h	**11**	0	99
5	**5**	**5** (5mmol); Bu_3P (10 mol %); Ac_2O (3 mL); 0 °C, 24 h	**11**	0	98
6	**5**	**5** (5 mmol); DMAP (10 mol %); Ac_2O (2 mL); pyridine (2 mL); 30 °C, 24 h	**11**	0	88
7	 (**6**)	**6** (5 mmol);**1a** (2 mol %); **3b** (5 mL); 40 °C; 69 h	 (**14**)	82	2
8	 (**7**)	**7** (3mmol);**1a** (9 mol %); **3a** (5 mL); 30 °C; 24 h	 (**15**)	93	0
9	 (**8**)	**8** (2 mmol);**1a** (1 mol %); **3a** (5 mL); 30 °C; 25 h	 (**16**)	97	0
10	 (**9**)	**9** (2 mmol);**1a** (5 mol %); **3b** (3 mL); 30 °C; 46 h	 (**17**)	96	2
11	 (**10**)	**10** (1 mmol);**1a** (2 mol %); **3a** (5 mL); THF (8 mL); 30 °C; 20 h	 (**18**)	84	4

We have already disclosed that various distannoxane-catalyzed reactions occurs under almost neutral conditions.[23] It is quite reasonable therefore to expect chemoselectivity in the present method. This is indeed the case as shown in Table 4. The acid-sensitive TBS and THP groups survived (entry 1 and 2). It is to be noted that both functions were replaced by the acetyl group to furnish the corresponding diacetates (96-97%) by the $Ac_2O/Sc(OTf)_3$ method. No sign of isomerization, cyclization and decomposition was observed for geraniol and furfuryl alcohol (entries 3 and 4). The base-sensitive trifluoroacetyl group also remained intact (entry 5) whereas Ac_2O/pyridine/DMAP furnished the diacetate, $AcO(CH_2)_4OAc$ (94%). The clean reaction took place with an α,β-acetylenic ester (entry 6) which suffered decomposition upon exposure to Bu_3P. The sulfinyl group was also employable (entry 7). When this substrate was subjected to the Ac_2O acetylation promoted by $Sc(OTf)_3$, pyridine/DMAP or Bu_3P, some byproducts were formed in every case and the yield was 79-93%. Notably, a disulfide linkage is completely tolerant (entry 8) to give a quantitative yield of the desired diacetate, $[AcO(CH_2)_2S]_2$. The $Sc(OTf)_3$ or Bu_3P/Ac_2O methods resulted in the cleavage of the S-S bond to give $AcS(CH_2)_2OAc$ in 97 and 96% yields, respectively.

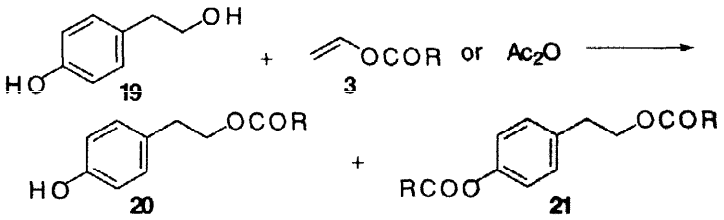
Table 4. Chemoselective Acylation[a]

Entry	2	1a (mol %)	Condition (°C, h)	4 (% yield)[b]
1	$TBSO(CH_2)_4OH$	1	30, 23	98
2	$THPO(CH_2)_4OH$	1	30, 23	97
3	geraniol	1	30, 22	98
4	furfuryl alcohol	3	30, 24	98
5	$CF_3CO_2(CH_2)_4OH$	1	30, 24	97
6	$PhOC(O)C{\equiv}CCH_2OH$	1	30, 24	97
7	$PhS(O)(CH_2)_6OH$	1	30, 23	97
8	$HO(CH_2)_2SS(CH_2)_2OH$	1	30, 24	98

[a] Reaction conditions: **2** (5 mmol), **3a** (5 mL). [b] Isolated yield after column chromatography.

The differentiation between phenol and primary alcohol has been the subject of considerable attention. Both normal preference of phenol over primary alcohol[22a,c,g] and the reversed preference[8,9,16a,22e,] were reported. The inertness of phenol disclosed in Table 2 gives promise of this type of discrimination. The primary hydroxyl was acylated in the presence of phenol (Table 5). When substrate **19** was exposed to vinyl esters, the desired primary esters **20** were produced exclusively in quantitative yields (entries 1-5). No such selectivity was realized by the three other methods (entries 6-8). It was reported that $Sc(OTf)_3$-catalyzed benzoylation of a 1:1 mixture of phenol and 3-phenyl-1-propanol furnished the corresponding benzoates in 8 and 91% yields, respectively.[8] However, no selectivity was attained for acetylation under similar conditions. Moreover, the $TMSOTf/Ac_2O$ variant was found to give a 93:7 **20/21** ratio after 3.5 days as a result of thermodynamic equilibration.[9] Notably, our method led to a quantitative yield of **20** with perfect selectivity after only 40 minutes in refluxing THF (entry 2).

Table 5. Differentiation between Primary Alcohol and Phenol



Entry	Reactn Condns	R	20 (% yield)	21 (% yield)
1	**19** (5 mmol); **1a** (5 mol %); **3a** (2.5 mL); THF (2.5 mL); 30 °C; 24 h	CH_3	99	0
2	**19** (5 mmol); **1a** (2 mol %); **3a** (2.5 mL); THF (2.5 mL); reflux, 40 min	CH_3	98	0
3	**19** (5 mmol); **1a** (10 mol %); **3c** (3 mL); THF (2.5 mL); 50 °C; 68 h	Ph	98	0
4	**19** (5 mmol); **1a** (10 mol %); **3d** (3 mL); CH_3CN (5 mL); 50 °C; 36 h	CH_2=CH	96	0
5	**19** (5 mmol); **1a** (10 mol %); **3e** (3 mL); CH_3CN (5 mL); 50 °C; 70 h	^{i}Bu	96	0
6	**19** (5 mmol); $Sc(OTf)_3$ (1 mol %); Ac_2O (3 mL); 30 °C; 4 h	CH_3	0	91
7	**19** (5 mmol); Bu_3P (10 mol %); Ac_2O (3 mL); 30 °C; 4 h	CH_3	0	95
8	**19** (5 mmol); DMAP (10 mol %); Ac_2O (2 mL); pyridine (2 mL); 30 °C; 24 h	CH_3	13	84

Finally, it has been revealed that distannoxane **1a** is also effective for acylation with Ac_2O (Table 6). Exposure of alcohols to Ac_2O (1.1-3.0 equiv) in the presence of a catalytic amount of **1a** afforded acetates. The reaction can be run both with and without solvent. In essence, the chemoselectivities hold in these cases as well since acid-sensitive groups remained intact.

Table 6. Distannoxane-Catalyzed Acetylation with Ac_2O.[a)]

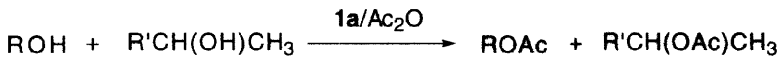
ROH + Ac_2O —**1a**→ ROAc

Entry	ROH	Ac_2O (equiv.)	Solvent	ROAc (% yield)[b)]
1	**2a**	3.0	none	96
2	**2a**	3.0	toluene	91
3	**2c**	1.1	none	90
4	$TBSO(CH_2)_4OH$	2.5[c)]	CH_3CN	89
5	$THPO(CH_2)_4OH$	2.5[d)]	CH_3CN	93

[a)] Reaction conditions: ROH (5 mmol); **1a** (0.05 mmol); solvent 5 mL; 30 °C; 24 h. [b)] Isolated yield. [c)] **1a** (5 mol %). [d)] **1a** (4 mol %).

The differentiation between primary and secondary alcohols was observed to some degree but the level of selectivity was not so high as that of the enol ester protocol (Scheme 2).

Scheme 2.[a,b]



2a	**2b**	[**1a** (10 mol %)[c]	89%	26%
2a	**2b**	[**1a** [4 mol %)][d]	85%	5%
2c	**2d**	[**1a** (1 mol %)][e]	80%	7%

[a] Reaction conditions: alcohols (5 mmol each); 30 °C; 24 h.
[b] Yields determined by GLC. [c] Ac_2O (5 mL). [d] Ac_2O (4.5 mmol).
[e] Ac_2O (5.5 mmol).

CONCLUSION

Acylation of alcohols by esters or Ac_2O is catalyzed by distannoxanes. In particular, the use of enol esters accelerates the reaction without violation of the innate mildness and, accordingly, a highly practical version has been advanced in terms of effective differentiation between primary/secondary alcohols or primary alcohol/phenol as well as of excellent chemoselectivity. The operation is quite simple. Mixing the reactants followed by evaporation gives the crude product; no aqueous workup is necessary. The catalyst can be removed by column chromatography or distillation when the product is distillable. Of great synthetic importance are the facile availability of the catalysts[26] and their stability towards hydrolysis and oxidation. Thus, enol esters and solvents can be used as received without purification and no inert atmosphere is necessary for the reaction. Consequently, the present method will find a wide spectrum of synthetic applications.

EXPERIMENTAL SECTION

General: All reactions were carried out in the open air. Ethyl acetate, isopropenyl acetate and other acetylation reagents were used without any purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetnitrile and pyridine were distilled from CaH_2. NMR spectra were recorded at 25 °C on Varian Gemini-300, JEOL Lambda 300 and JEOL Lambda 500 spectrometers and calibrated with tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded on a Jeol MStation JMS-700 spectrometer. Elemental analyses were performed with Perkin Elmer PE 2400. Melting points were determined with a Yanaco micro melting point apparatus and were uncorrected. Silica gel (Daiso gel IR-60) was used for column chromatography. GC analyses were performed using a capilally column of CBP1-M25 with SHIMADZU GC-17A.

Preparation of distannoxane 1: Distannoxanes **1a**, **1b**, **1c** and **1d** were prepared according to literature methods but our most recent trials giving rise to higher yields are described below.

1a:[27] A benzene suspension (60 mL) of Bu_2SnO (7.47 g, 30.0 mmol) and Bu_2SnCl_2 (9.11 g, 30 mmol) was heated at reflux for 7 h. After evaporation and addition of dichloromethane, insoluble solids were separated from the solution by filtration on a celite pad, and the filtrate was concentrated under reduced pressure. A crude mixture was recrystallized from hexane to give a white solid **1a** (15.9 g, 96%), m.p. 109-112 °C (lit. 107-108 °C).

1b:[28] A 95% ethanol suspension (30 mL) of **1a** (11.0 g, 20.0 mmol) and sodium thiocyanate (3.57 g, 44 mmol) was heated at reflux for 7 h. After evaporation and addition of dichloromethane, insoluble solids were separated from the solution by filtration on a celite pad, and the filtrate was concentrated under reduced

pressure. A crude mixture was recrystallized from hexane to give colorless needles **1b** (8.0 g, 69%), m.p. 86-89 °C (lit. 83.5-84.5 °C).

1c:[27] A 95 % ethanol suspension (60 mL) of Bu_2SnO (14.93 g, 60.0 mmol) and Bu_2SnCl_2 (6.08 g, 20 mmol) was heated at reflux for 7 h. After evaporation and addition of dichloromethane, insoluble solids were separated from the solution by filtration on a celite pad, and the filtrate was concentrated under reduced pressure. A crude mixture was recrystallized from hexane to give a white solid **1c** (20.3 g, 95%), m.p. 101-110 °C (lit. 109-121 °C).

1d:[28] A 95% ethanol suspension (40 mL) of **1c** (5.34 g, 10.0 mmol) and sodium thiocyanate (1.62 g, 20 mmol) was heated at reflux for 7 h. After evaporation and addition of dichloromethane, insoluble solids were separated from the solution by filtration on a celite pad, and the filtrate was concentrated under reduced pressure. A crude mixture was recrystallized from hexane to give a white solid **1d** (3.9 g, 70%), m.p. 118-129 °C [lit. 123-134 °C (Dec)].

The following acetates are known compounds, and the spectral data of these compounds agreed with those in the literature: 2-phenylethyl acetate,[29] 1-phenylethyl acetate,[30] 1-octyl acetate,[18] 1-octyl benzoate,[18] 1-octyl acrylate,[18] 1-octyl pivalate,[18] 1-octyl chloroacetate,[18] 2-octyl acetate,[31] benzyl acetate,[32] 1-acetoxy-5-hydroxyhexane (**11**),[33] **14**,[34] **16**,[35] **18**,[36] 1-acetoxy-2-hydroxyoctane,[37] 2-acetoxy-1-hydroxyoctane,[37] 1,2-diacetoxyoctane,[37] geranyl acetate,[38] furfuryl acetate,[39] bis(2-acetoxyethyl) disulfide,[40] 2-(4-hydroxyphenyl)ethyl acetate,[41] 2-(4-acetoxyphenyl)ethyl acetate.[42]

Acetylation of alcohol with ethyl acetate catalyzed by distannoxane (representative): An ethyl acetate solution (10 mL) of 2-phenylethanol (**2a**) (611 mg, 5.0 mmol) and distannoxane **1a** (138.2 mg, 0.25 mmol) was heated at reflux for 12 h. After evaporation, residue was subjected to column chromatography on silica gel to give 2-phenethyl acetate (772 mg, 93%).

Acylation of alcohol with vinyl acetate catalyzed by distannoxane (representative): A vinyl acetate (**3a**) solution (5 mL) of **2a** (611 mg, 5.0 mmol) and **1a** (138.2 mg, 0.25 mmol) was stirred at 30 °C for 5 h. After evaporation, the residue was subject to column chromatography on silica gel to give 2-phenethyl acetate (788 mg, 96%).

Acylation of 1,5-hexandiol (5) with isopropenyl acetate catalyzed by distannoxane (representative): An isopropenyl acetate (**3b**) solution (5 mL) of **5** (355 mg, 3.0 mmol) and **1a** (33.2 mg, 0.06 mmol) was stirred at 30 °C for 24 h. After evaporation, the residue was subjected to column chromatography on silica gel to give acetate **11** (449 mg, 93%).

Acetylation of 5 catalyzed by $Sc(OTf)_3$: An acetic anhydride solution (3 mL) of **5** (591.0 mg, 5.0 mmol) and scandium triflate (24.6 mg, 0.05 mmol) was stirred at 30 °C for 24 h. After usual work-up with aqueous sodium hydrogen carbonate solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subjected to column chromatography to give 1,5-di(acetoxy)hexane (999.1 mg, 99%).

Acetylation of 5 catalyzed by Bu_3P: An acetic anhydride solution (3 mL) of **5** (591.0 mg, 5.0 mmol) and tributylphosphine (101.2 mg, 0.5 mmol) was stirred at 0 °C for 24 h. After usual work-up with aqueous ammonium chloride solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subjected to column chromatography to give 1,5-di(acetoxy)hexane (991.0 mg, 4.9 mmol, 98%).

Acetylation of 5 catalyzed by pyridine/DMAP: An acetic anhydride (2 mL) and pyridine (2 mL) solution of **5** (591.0 mg, 5.0 mmol) and 4-(dimethylamino)pyridine (61.1 mg, 0.5 mmol) was stirred at 30 °C for 24 h. After usual work-up with aqueous ammonium chloride solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subject to column chromatography to give 1,5-di(acetoxy)hexane (889.9 mg, 88%).

12: ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J = 6.2 Hz, 3H), 1.40-1.90 (m, 7H), 3.77-3.89 (m, 1H), 4.33 (t, J = 6.6 Hz, 2H), 7.39-7.48 (m, 2H), 7.50-7.60 (m, 1H), 8.00-8.09 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.0, 23.2, 28.5, 38.5, 64.7, 67.4, 128.1 (2C), 129.3 (2C), 130.1, 132.6, 166.5; HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1239.

13: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 6.2 Hz, 3H), 1.26-1.78 (m, 7H), 3.72-3.90 (m, 1H), 4.17 (t, J = 6.6 Hz, 2H), 5.82 (d, J = 10.4 Hz, 1H), 6.12 (dd, J = 10.4, 17.4 Hz, 1H), 6.41 (d, J = 17.4 Hz, 1H); ^{13}C NMR ($CDCl_3$)

δ 22.1, 23.4, 28.5, 38.6, 64.4, 67.7, 128.4, 130.5, 166.3; HRMS (FAB) *m/e* calcd for $C_9H_{17}O_3$ (M^++1) 173.1178, found 173.1171.

15 (a mixture of diastereomers): ^{1}H NMR ($CDCl_3$) δ 0.76-2.03 (m, 14H), 2.05 (s, 3H), 3.11-3.31, 3.85-3.94 (m, 1H), 4.06 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.0, (20.4), 24.8, (21.0), 25.4, (25.1), 25.7, (26.1), 28.4, (26.5), 30.1, (28.1), 35.8, (33.1), 44.7, (40.9), 64.9, (64.8), 74.5, (69.1), 171.3, (171.3); HRMS (EI) *m/e* calcd for $C_{11}H_{20}O_3$ 200.1412, found 200.1418.

17: ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9H), 1.40-1.90 (m, 4H), 2.04 (s, 3H), 2.55, 2.68 (ABX, J_{AB} = 19.7, J_{AX} = 10.0, J_{BX} = 2.9 Hz, 2H), 3.33 (s, 1H), 3.98-4.04 (m, 1H), 4.09 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.0, 24.8, 26.2 (3C), 32.7, 43.0, 44.3, 64.4, 67.3, 171.2, 217.7; HRMS (FAB) *m/e* calcd for $C_{12}H_{23}O_4$ (M^++1) 231.1596, found 231.1607.

Acetylation of 1,2-octanediol with isopropenyl acetate catalyzed by distannoxane (representative): An isopropenyl acetate (**3b**) solution (5 mL) of 1,2-octanediol (731.2 mg, 5.0 mmol) and **1a** (276.7 mg, 0.5 mmol) was stirred at 40 °C for 50 h. After evaporation, methanol was added to the residue, and the solution was filtered through a celite pad. The residue obtained by evaporation was subjected to GC analysis (monoacetate 31% yield, diacetate 24% yield). The ratio of primary and secondary monoacetates was determined by ^{1}H NMR after isolation by column chromatography on silica gel.

Acetylation of alcohol having a functional group with vinyl acetate catalyzed by distannoxane (representative): A vinyl acetate (**3a**) solution (5 mL) of 4-(*t*-butyldimethylsilyloxy)-1-butanol (1022.0 mg, 5.0 mmol) and **1a** (27.6 mg, 0.05 mmol) was stirred at 30 °C for 23 h. After evaporation, the residue was subjected to column chromatography on silica gel to give 1-acetoxy-4-(*t*-butyldimethylsilyloxy)butane (1207.4 mg, 4.9 mmol, 98%).

1-Acetoxy-4-(*t*-butyldimethylsilyloxy)butane: ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6H), 0.89 (s, 9H), 1.50-1.77 (m, 4H), 2.05 (s, 3H), 3.64 (t, J = 6.2 Hz, 2H), 4,08 (t, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -5.45 (2C), 18.2, 20.8, 25.1, 25.8 (3C), 29.1, 62.4, 64.3, 171.0; HRMS (FAB) *m/e* calcd for $C_{12}H_{27}O_3Si$ (M^++1) 247.1729, found 247.1731.

Tetrahydro-2-(4-acetoxybutoxy)-2*H*-pyrane: ^{1}H NMR ($CDCl_3$) δ 1.42-1.93 (m, 10H), 2.05 (s, 3H), 3.37-3.56 (m, 2H), 3.72-3.92 (m, 2H), 4.10 (t, J = 6.3 Hz, 2H), 4,58 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.0, 20.3, 25.0, 25.1, 25.7, 30.2, 61.5, 63.7, 66.3, 98.1, 170.3; HRMS (FAB) *m/e* calcd for $C_{11}H_{21}O_4$ (M^++1) 217.1440, found 217.1434.

4-Trifluoroacetoxybutyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.64-1.98 (m, 4H), 2.23 (s, 3H), 4.12 (t, J = 6.2Hz, 2H), 4,40 (t, J = 6.3Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.3, 24.5, 24.6, 63.2, 67.4, 114.3 (q, $^1J_{C\text{-}F}$ = 285.4 Hz), 157.1 (q, $^2J_{C\text{-}F}$ = 42.1 Hz), 170.6; HRMS (FAB) *m/e* calcd for $C_8H_{12}F_3O_4$ (M^++1) 229.0688, found 229.0694.

3-Phenoxycarbonyl-2-propynyl acetate: ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H), 4.86 (s, 2H), 7.12-7.15 (m, 2H), 7.25-7.29 (m, 1H), 7.36-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5, 51.2, 77.6, 84.0, 121.2 (2C), 126.5, 129.6 (2C), 149.7, 151.1, 169.8; HRMS (EI) *m/e* calcd for $C_{12}H_{10}O_4$ 218.0579, found 218.0568.

6-Phenylsulfinylhexyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.22-1.89 (m, 8H), 1.96 (s, 3H), 2.73 (t, J = 7.6 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 7.41-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.9, 25.5, 28.2 (2C), 56.9, 64.1, 123.9 (2C), 129.1 (2C), 130.9, 143.7, 171.1; HRMS (FAB) *m/e* calcd for $C_{14}H_{21}O_3S$ (M^++1) 269.1211, found 269.1212.

Acylation of 2-(4-hydroxyphenyl)ethanol (19) with vinyl acetate catalyzed by distannoxane (representative): A solution of **19** (690.8 mg, 5.0 mmol) and **1a** (138.2 mg, 0.25 mmol) in THF (2.5 mL) and **3a** (2.5 mL) was stirred at 30 °C for 24 h. After evaporation, the residue was subjected to column chromatography on silica gel to give 2-(4-hydroxyphenyl)ethyl acetate (**20**) (892.0 mg, 99%).

Acetylation of 19 with Sc(OTf)$_3$: An acetic anhydride solution (3 mL) of **19** (690.8 mg, 5.0 mmol) and scandium triflate (24.6 mg, 0.05 mmol) was stirred at 30 °C for 4 h. After usual work-up with aqueous sodium hydrogen carbonate solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subject to column chromatography to give 2-(4-acetoxyphenyl)ethyl acetate (**21**) (1011.0 mg, 91%).

Acetylation of 19 with Bu$_3$P: An acetic anhydride solution (3 mL) of **19** (690.8 mg, 5.0 mmol) and tributylphosphine (101.2 mg, 0.5 mmol) was stirred at 30 °C for 4 h. After usual work-up with aqueous ammonium chloride solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subject to column chromatography to give **21** (1055.5 mg, 95%).

Acetylation of 19 with pyridine/DMAP: A solution of **19** (690.8 mg, 5.0 mmol) and 4-(dimethylamino)pyridine (61.1 mg, 0.5 mmol) in acetic anhydride (2 mL) and pyridine (2 mL) was stirred at 30 °C for 24 h. After usual work-up with aqueous ammonium chloride solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subject to column chromatography to give **20** (117.1 mg, 13 %) and **21** (933.2 mg, 84%).

2-(4-Hydroxyphenyl)ethyl benzoate: ^{1}H NMR ($CDCl_3$) δ 2.97 (t, J =7.0 Hz, 2H), 4.48 (t, J = 7.0 Hz, 2H), 6.57 (br, 1H), 6.73-6.87 (m, 2H), 7.06-7.14 (m, 2H), 7.34-7.45 (m, 2H), 7.48-7.57 (m, 1H), 7.96-8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 34.2, 66.0, 115.4 (2C), 128.3 (2C), 129.4, 129.5 (2C), 129.9, 130.0 (2C), 133.1, 154.4, 167.2; HRMS (EI) *m/e* calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0928.

2-(4-Hydroxyphenyl)ethyl acrylate: ^{1}H NMR ($CDCl_3$) δ 2.52 (br, 1H), 2.89 (t, J = 7.0 Hz, 2H), 4.32 (t, J =7.0 Hz, 2H), 5.82 (dd, J = 1.4, 10.3 Hz, 1H), 6.10 (dd, J = 10.3, 17.3 Hz, 1H), 6.39 (dd, J = 1.4, 17.3 Hz, 1H), 6.75-6.82 (m, 2H), 7.02-7.09 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 34.1, 65.5, 115.4 (2C), 128.2, 129.2, 129.9 (2C), 131.2, 154.6, 166.8; HRMS (EI) *m/e* calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0772.

2-(4-Hydroxyphenyl)ethyl pivalate: ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 9H), 1.79 (br, 1H), 2.85 (t, J = 7.0 Hz, 2H), 4.23 (t, J = 7.0 Hz, 2H), 6.74-6.82 (m, 2H), 7.02-7.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.1 (3C), 34.1, 38.7, 65.4, 115.3 (2C), 129.5, 130.0 (2C), 154.6, 179.3; HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_2$ 222.1256, found 222.1263.

Acetylation with acetic anhydride catalyzed by distannoxane (representative): An acetic anhydride solution (1.4 mL, 15 mmol) of **2a** (611 mg, 5.0 mmol) and **1a** (27.6 mg, 0.25 mmol) was stirred at 30 °C for 24 h. After usual work-up with aqueous sodium hydrogen carbonate solution and ethyl acetate, the organic layer was dried over magnesium sulfate and evaporated. The crude mixture was subjected to column chromatography to give phenethyl acetate (788 mg, 96%).

REFERENCES

1. Litvinenko, L. M.; Kirichenko, A. I. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1967**, *176*, 97. Steglich, W.; Höfle, G. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 981. For a review: Höfle, G.; Steglich, W.; Vorbrügen, H. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569.
2. Höfle, G.; Steglich, W. *Synthesis* **1972**, 619. Hassner, A.; Krepski, L. R.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069. Inanaga, J.; Hirota, K.; Saeki, H.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1989. Shimizu, T.; Kobayashi, R.; Ohmori, H.; Nakata, T. *Synlett* **1995**, 650. Vedejs, E.; Chen, X. *J. Am. Chem. Soc.* **1996**, *118*, 1809. Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492. Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794. Garrett, C. E.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7479. Kawabata, T.; Nagato, M.; Takasu, K.; Fuji, K. *J. Am. Chem. Soc.* **1997**, *119*, 3169.
3. Vedejs, E.; Diver, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 3358. Vedejs, E.; Bennett, N. S.; Conn, L. M.; Diver, S. T.; Gingras, M.; Lin, S.; Oliver, P. A.; Peterson, M. J. *J. Org. Chem.* **1993**, *58*, 7268. Vedejs, E.; Daugulis, O.; Diver, S. T. *J. Org. Chem.* **1996**, *61*, 430.
4. D'Sa, B. A.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963.
5. Cope, A. C.; Herrick, E. C.*Org. Synth.* **1963**, *4*, 304.
6. Baker, R. H.; Bordwell, F. G. *Org. Synth.* **1955**, *3*, 141.
7. Iqbal, J.; Scrivastava, R. R. *J. Org. Chem.* **1992**, *57*, 2001.
8. Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1995**, *117*, 4413; *J. Org. Chem.* **1996**, *61*, 4560.
9. Procopiou, P.A.; Baugh, S. P. D.; Falck, S. S.; Inglis, G. G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2625; *J. Org. Chem.* **1998**, *63*, 2342.
10. Chandrasekhan, S.; Ramachander, T.; Takhi, M. *Tetrahedron Lett.* **1998**, *39*, 3263.
11. Li, A.-I.; Li, T.-S.; Ding, T.-H. *J. Chem. Soc., Chem. Commun.* **1997**, 1389.
12. Ballini, R.; Bosica, G.; Carloni, S.; Ciaralli, L.; Maggi, R.; Sartori, G. *Tetrahedron Lett.* **1998**, *39*, 6049.
13. Vedejs, E.; Daugulis, O. *J. Org. Chem.* **1996**, *61*, 5702.
14. Kammoun, K.; Le Biot, Y.; Delmas, M.; Boutevin, B. *Synth. Commun.* **1997**, *27*, 2777.
15. Otera, J. *Chem. Rev.* **1993**, *93*, 1449.

16. a) Pereyre, M.; Colin, G.; Delvigne, J.-P. *Bull. Soc. Chim. Fr.* **1969**, 262. b) Posner, G. H.; Oda, M. *Tetrahedron Lett.* **1981**, *22*, 5003. c) Rana, S. S.; Barlow, J. J.; Matta, K. L. *Tetrahedron Lett.* **1981**, *22*, 5007. d) Seebach, D.; Hungerbühler, E.; Naef, R.; Schnurrenberger, P.; Weidmann, B.; Züger, M. *Synthesis*, **1982**, 138. Imwinkelried, R.; Schiess, M.; Seebach, D. *Org. Synth.* 1993, Coll. Vol. 8, 201. e) Kasik, P. *Tetrahedron Lett.* **1998**, *39*, 4233. f) Nishiguchi, T.; Taya, H. *J. Am. Chem. Soc.* **1989**, *111*, 9102. g) Breton, G. W. *J. Org. Chem.* **1997**, *62*, 8952. h) Okano, T.; Miyamoto, K.; Kiji, J. *Chem. Lett.* **1995**, 246. i) Furlán, R. L. E.; Mata, E. G.; Mascaretti, O. A. *Tetrahedron Lett.* **1998**, *39*, 2257. j) Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1998**, *28*, 1923.
17. Hagemeyer, H. J. Jr.; Hull, D. C. *Ind. Eng. Chem.* **1949**, *41*, 2920. Rothman, E.; Hecht, S.; Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1972**, *37*, 3551. Kita, Y.; Maeda, H.; Takahashi, F.; Fukui, S. *J. Chem. Soc., Chem. Commun.* **1993**, 410. Kita, Y.; Maeda, H.; Omori, K.; Okuno, T.; Tamura, Y. *J. Chem. Soc. Perkin Trans. 1* **1993**, 2999.
18. Ishii, Y.; Takeno, M.; Kawasaki, Y.; Muromachi, A.; Nishiyama, Y.; Sakaguchi, S. *J. Org. Chem.* **1996**, *61*, 3088.
19. a) Norris, J. F.; Rigby, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 2088. b) Abramovitch, B.; Schivers, J. C.; Hudson, B. E.; Hauser, C. R. *J. Am. Chem. Soc.* **1943**, *65*, 986. d) Newman, M. S.; Lala, L. K.; *Tetrahedron Lett.* **1967**, 3267. e) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 3971. f) Ogawa, H.; Amano, M.; Chihara, T. *J. Chem. Soc., Chem. Commun.* **1998**, 495.
20. Shiina, I.; Miyoshi, S.; Miyashita, M.; Mukaiyama, T. *Chem. Lett.* **1994**, 515. Izumi, J.; Shiina, I.; Mukaiyama, T. *Chem. Lett.* **1995**, 141.
21. Bianco, A.; Brufani, M.; Melchioni, C.; Romagnoli, P. *Tetrahedron Lett.* **1997**, *38*, 651.
22. a) Oazi, O. O.; Corral, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 2162. b) Steglich, W.; Hölfe, G. *Tetrahedron Lett.* **1970**, 4727. c) Mukaiyama, T.; Pai, F.-C.; Onaka, M.; Narasaka, K. *Chem. Lett.* **1980**, 563. d) Sekine, M.; Kume, A.; Hata, T. *Tetrahedron Lett.* **1981**, 22, 3617. e) Kunieda, T.; Mori, T.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett.* **1985**, *26*, 1977. f) Kim, S.; Chang, H.; Kim, W. J. *J. Org. Chem.* **1985**, *50*, 1751. g) Paradisi, M. P.; Zechhini, G. P.; Torrini, I. *Tetrahedron Lett.* **1986**, *27*, 5029. h) Yamada, S. *J. Org. Chem.* **1992**, *57*, 1591. i) Yamada, S.; Sugaki, T.; Matsuzaki, K. *J. Org. Chem.* **1996**, *61*, 5932. j) Evans, D. A.; Anderson, J. C.; Taylor, M. K. *Tetrahedron Lett.* **1993**, *34*, 5563.
23. Otera, J. In *Advances in Detailed Reaction Mechanisms*, J.M. Coxon, Ed., JAI Press Inc., London, 1994, Vol. 3, p167.
24. For a preliminary communication: Orita, A.; Mitsutome, A.; Otera, J. *J. Org. Chem.* **1998**, *63*, 2420.
25. Otera, J.; Yano, T.; Kawabata, H.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2383. Otera, J.; Dan-oh, N.; Nozaki, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1742; *J. Org. Chem.***1991**, *56*, 5307.
26. See experimental section and **1a** is now commercially available from Aldrich Chemical Co., Inc.
27. Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81.
28. Wada, M.; Nishino, M.; Okawara, R. *J. Organomet. Chem.* **1965**, *3*, 70.
29. Fuji, K.; Node, K.; Kawabata, T.; Fujimoto, M. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1043.
30. Laumen, K.; Schneider, M. P. *J. Chem. Soc. Chem. Commun.* **1988**, 598.
31. Franzyshen, S. K.; Schiavelli, M. D.; Stocker, K. D.; Ingram, M. D. *J. Phys. Chem.* **1990**, *94*, 2684.
32. Masnovi, J.; Maticic, J. *J. Am. Chem. Soc.* **1988**, *110*, 5189.
33. Posner, G. H.; Oda, M. *Tetrahedron. Lett.* **1981**, *22*, 5003.
34. Ahmad, S.; Iqbal, J. *J. Chem. Soc. Chem. Commun.* **1987**, 114.
35. Yeh, M. C. P.; Knochel, P.; Santa, L. E. *Tetrahedron. Lett.* **1988**, *29*, 3887.
36. Paradisi, M. P.; Zecchini, G. P.; Torrini, I. *Tetrahedron Lett.* **1986**, *27*, 5029.
37. Uemura, S.; Ohe, K.; Fukuzawa, S.-I.; Patil, S. R.; Sugita, N. *J. Organomet. Chem.* **1986**, *316*, 67.
38. Badet, B.; Julia, M.; Mallet, J. M.; Schmitz, C. *Tetrahedron* **1988**, *44*, 2913.
39. Torii, S.; Tanaka, H.; Tsutsui, Y.; Ohshima, T.; Yamashita, S. *Chem. Lett.* **1986**, 1535.
40. Sato, T.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1990**, *31*, 3595.
41. Endo, K.; Seya, K.; Hikino, H. *Tetrahedron* **1989**, *45*, 3673.
42. Breton, J. L.; Llera, L. D.; Navarro, E.; Trujillo, J. *Tetrahedron* **1987**, *43*, 4447.