Organic LETTERS

Lewis Base Activation of Silyl Acetals: Iridium-Catalyzed Reductive Horner–Wadsworth–Emmons Olefination

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Supporting Information

ABSTRACT: A Lewis base promoted deprotonative pronucleophile addition to silyl acetals has been developed and applied to the iridium-catalyzed reductive Horner–Wadsworth–Emmons (HWE) olefination of esters and the chemoselective reduction of the resulting enoates. Lewis base activation of silyl acetals generates putative pentacoordinate silicate acetals, which fragment into aldehydes, silanes, and alkoxides in situ. Subsequent deprotonative metalation of phosphonate esters followed by HWE with aldehydes furnishes enoates. This operationally convenient, mechanistically unique protocol converts the traditionally challenging aryl, alkenyl, and alkynyl esters to homologated enoates at room temperature within a single vessel.

Acetals **1**, metal acetals **2**, and silyl acetals **3** can serve as aldehyde equivalents in organic synthesis (Figure 1).

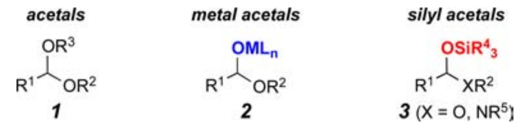

Figure 1. Various acetals.

Acetals **1** are acid-labile/base-stable, whereas metal acetals **2** are only reasonably stable at low temperature. On the other hand, silyl acetals **3** are tetrahedral intermediate mimics which are reasonably stable even at elevated temperatures, yet are acid- and silaphile-labile. Mukaiyama,[1] Tietze,[2] and Oshima[3] demonstrated mixed *O*,*O*-silyl acetals and their synthetic applications; these were predominantly exploited for Lewis acid catalyzed allylsilane additions. Nonetheless, silyl acetals have seen limited application in synthetic chemistry so far.[4]

Reductive Horner–Wadsworth–Emmons (HWE) strategies involving the in situ generation of the **2**/nucleophilic capture have been developed by Takacs,[5a] Burton,[5b] and Hoye[5c] (Scheme 1a).[6,7] Although these approaches have been successful, they are restricted in substrate scope due to the inherent instability of metal acetals. Consequently, the carbonyl substituents are primarily alkyl in nature, in addition to a limited number of aryl and alkenyl substituents—to the best of our knowledge, no example pertaining to alkynyl esters has been reported. Trost and Herzon demonstrated that the single-pot HWE olefination of challenging enals is viable at −90 or −95 °C.[8] Alternatively, the An group developed lithium diisobutyl-*tert*-butoxyaluminum hydride and other congeners, which improve the stability of the aluminum acetals (typically below 0 °C).[9]

To develop useful synthetic transformations utilizing silyl acetals directly as aldehyde equivalents and understand their reactivity, we envisioned the application of Lewis base promoted deprotonative pronucleophile addition reactions to **3** (Scheme 1b).[10] Specifically, such substrates **3** can be generated through Ir-catalyzed hydrosilylation of esters **4**.[11,12] Subsequent nucleophilic attack of the Lewis base (LB) on **3** generates putative pentacoordinate silicate acetals **6**,[13,14] which are likely to fragment into silanes **7**, aldehydes **8**, and alkoxides **9**. Subsequent deprotonative metalation of pronucleophiles, with an anion-stabilizing group, by **9** yields a metalated pronucleophile anion, which in turn traps aldehydes **8** to furnish alcohols **10**.

We report a Lewis base promoted deprotonative pronucleophile addition to silyl acetals, an application to a single-pot Ir-catalyzed reductive HWE olefination at rt as an alternative to the traditional HWE olefination (Scheme 1c). Initial dialkylhydridosilyl acetals **3**, produced via Ir-catalyzed ester hydrosilylation, are available for the HWE reaction upon addition of appropriate Lewis bases and phosphonate esters (i.e., pronucleophile). Advantages of this single-pot Ir-catalyzed reductive HWE olefination approach are 4-fold: (1) This approach can be carried out under mild reaction conditions (e.g., at rt). (2) The experimental procedure is substantially simpler than that of aluminum hydride based reductive homologation method by virtue of in situ generation of **8** and **9** via a fragmentation of silyl acetals, thus avoiding the need for premetalation of nucleophiles. (3) This catalytic reductive method allows direct conversion of traditionally challenging aryl esters, enoates, and ynoates to corresponding homologated esters. (4) Due to use of a substoichiometric amount of Ir catalyst (0.1 mol %), the reactions are feasible for a range of scales from subgram to gram quantities of the esters.

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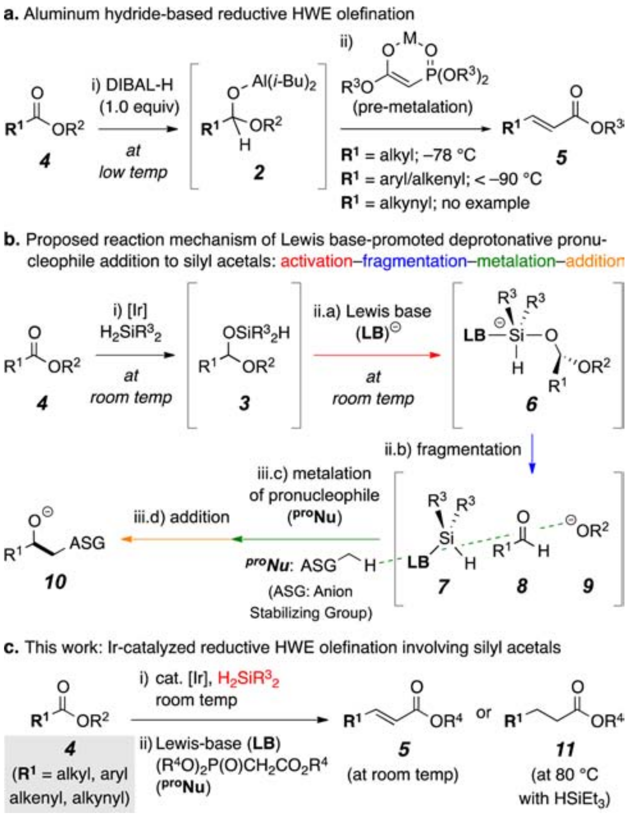
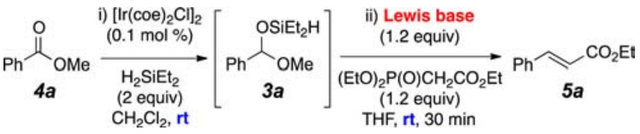
Scheme 1. Design for the Reductive HWE Olefination Involving Silyl Acetals



Diethylhydridosilyl acetal **3a** was conveniently prepared through the hydrosilylation of ester **4a** with the iridium catalyst $[Ir(coe)_2Cl]_2$ (0.1 mol %) and diethylsilane (2 equiv) (Table 1).[11,15] The resulting silyl acetal **3a** functions as a stable metal acetal species. We then studied the impact of Lewis base upon the single-pot reductive HWE reaction. When **3a** was subjected to HWE reaction conditions without purification, Lewis bases such as TBAF, NaOEt, NaO*t*-Bu, and KO*t*-Bu (1.2 equiv) provided enoate **5a** in moderate yields (entries 1–4). Interestingly, metal trimethylsilanoates (entries 5–7) as Lewis bases afforded **5a** in excellent yield (84–95% NMR yield) and high stereoselectivity (>20:1 *E*/*Z*). $KOSiMe_3$ was identified as the best Lewis base for the Lewis base promoted reductive HWE reaction (87% isolation yield, entry 7).[16,17]

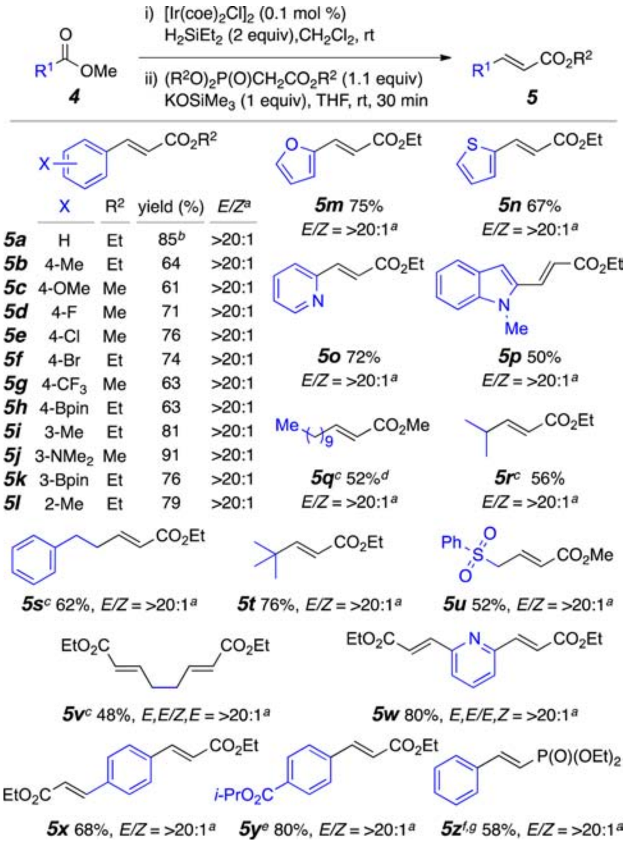
Table 1. Study of Lewis Base for Single-Pot Ir-Catalyzed Reductive HWE Olefination[a]



entry	Lewis base	yield of **5a** (%)[b]	*E*/*Z* (**5a**)[c]
1	TBAF	26	>20:1
2	NaOEt	33[d] (69)[e]	>20:1
3	NaO*t*-Bu	28[d] (76)[e]	>20:1
4	KO*t*-Bu	66[d] (80)[e]	>20:1
5	$LiOSiMe_3$	84	>20:1
6	$NaOSiMe_3$	85	>20:1
7	$KOSiMe_3$	95 (87)[f]	>20:1

[a] Conditions: **4a** (0.2 mmol), (i) CH_2Cl_2 (3.3 M); (ii) THF (0.1 M). [b] Determined by ^1H NMR spectroscopy utilizing an internal standard (CH_2Br_2). [c] Determined by ^1H NMR spectroscopy. [d] No completion was observed after 48 h. [e] With 3 equiv of Lewis base. [f] Isolated yield.

Scheme 2. Scope of Aromatic and Acyclic Esters for Single-Pot Ir-Catalyzed Reductive HWE Olefination



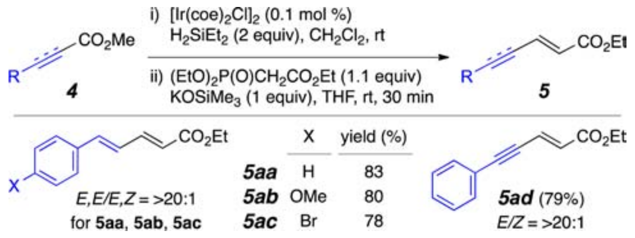
	X	R^2	yield (%)	*E*/*Z*[a]
5a	H	Et	85[b]	>20:1
5b	4-Me	Et	64	>20:1
5c	4-OMe	Me	61	>20:1
5d	4-F	Me	71	>20:1
5e	4-Cl	Me	76	>20:1
5f	4-Br	Et	74	>20:1
5g	4-CF_3	Me	63	>20:1
5h	4-Bpin	Et	63	>20:1
5i	3-Me	Et	81	>20:1
5j	3-NMe_2	Me	91	>20:1
5k	3-Bpin	Et	76	>20:1
5l	2-Me	Et	79	>20:1

[a] Determined by ^1H NMR spectroscopy. [b] Reaction of **1a** on 10 mmol scale. [c] Saturated esters (ca. 3:1 of **5**/saturated **5**) were produced. [d] Combined yields of **5q**/saturated **5q** (6:1). [e] H_2Si*i*-Pr_2 (1.2 equiv) was used. [f] Tetraethyl methylenediphosphonate was used as a pronucleophile. [g] Reaction at rt for 2 h.

Based on these encouraging initial results, we probed the substrate scope for the single-pot catalytic reductive HWE olefination at rt (Scheme 2).[18] The *ortho*-, *meta*-, and *para*-substituted aromatic esters afforded the corresponding enoates (**5b–l**) with good to excellent yields and excellent *E*/*Z* ratios (>20:1). For example, the reaction of methyl benzoate on 10 mmol scale afforded **5a** in 85% yield. Heterocycles such as furan, thiophene, pyridine, and indole also tolerated the reaction conditions to provide **5m–p**. Reactions with aliphatic esters afforded enoates **5q–s** with excellent *E*/*Z* ratios, albeit with somewhat diminished yields due to competitive olefin saturation (ca. 3:1 of **5**/saturated **5**). Hindered methyl pivalate gave **5t** with good yield and excellent stereoselectivity. This method would be particularly useful for cases in which the isolation of aldehydes is impractical, due to the instability or inconvenience of the necessary operation involved with separation. Reductively generated phenylsulfonylacetaldehyde from methyl phenylsulfonylacetate was notoriously difficult to isolate and tends to decompose by methods employing either extraction or chromatography.[11] Our developed reductive HWE reaction of methyl phenylsulfonylacetate afforded the corresponding enoate **5u** with 52% yield and excellent stereoselectivity. Bidirectional addition of nucleophiles to succinaldehyde has been challenging due to its instability and intramolecular engagement of initially produced metal alkoxide with the appended aldehyde to form a cyclic acetal adduct.[5c] Bidirectional reductive HWE using diethyl succinate, diethylpyridine-2,6-dicarboxylate, and diethyl terephthalate under the identical conditions allowed access to dienoates **5v**, **5w**, and **5x**, respectively. Chemoselective reductive HWE olefination of isopropyl methyl terephthalate provided monohomologated enoate **5y**, which is difficult to achieve through traditional reductive HWE tactics. Finally, when a bisphosphonate as a pronucleophile was employed, vinylphosphonate **5z** was produced in moderate yield.

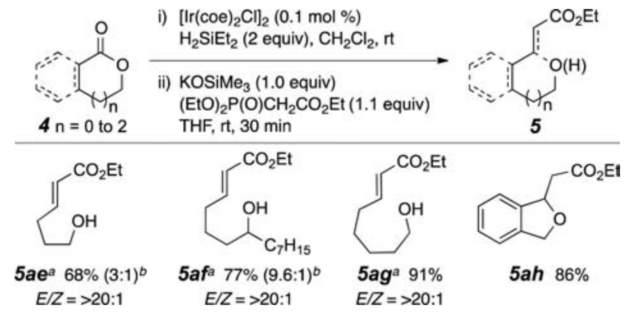
Next, challenging enoates and ynoate substrates were examined (Scheme 3). We achieved the catalytic reductive HWE reactions of α,β-unsaturated esters at rt, which afforded the corresponding dienoates **5aa−ac** and ynenoates **5ad** with good yields and excellent *E,E*/*E,Z* ratios.

Scheme 3. Scope of Enoates and Ynoates



We then studied sequential reductive HWE (and cycloetherification) of lactones (Scheme 4). Substrates differing in ring size afforded hydroxy enoates **5ae−ag** with excellent *E*/*Z* ratios and good yields, along with minor saturated esters and cycloetherification products. Particularly, benzolactone spontaneously underwent cycloetherification after reductive HWE reaction, which furnished **5ah**.

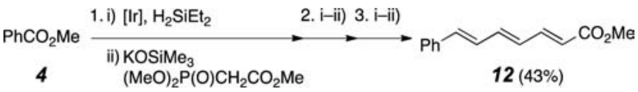
Scheme 4. Scope of Lactones for Sequential Reductive HWE (and Cycloetherification)



[a]Saturated esters (<5%) were produced. [b]Ratio of hydroxy enoates/cycloetherification products.

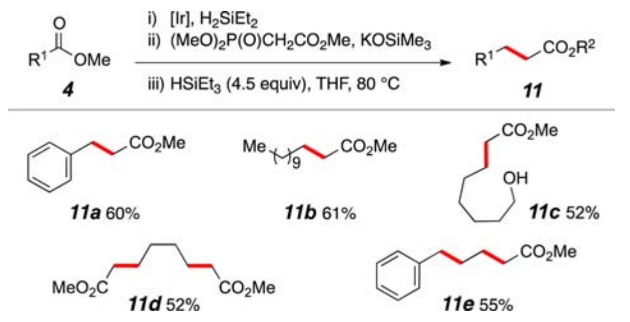
We also investigated iterative reductive HWE olefination of silyl acetals (Scheme 5). Traditional methods for the synthesis of trienoate **12** require three iterations of a three-step reduction, oxidation, and HWE sequence (a total of 9 linear steps). A triply iterated, single-pot catalytic reductive HWE reaction provided (2*E*,4*E*,6*E*)-trienoates **12** with 43% yield.

Scheme 5. Iterative Reductive HWE Olefination



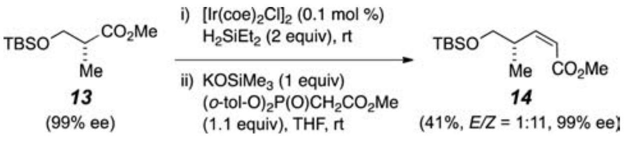
Furthermore, single-pot Ir-catalyzed reductive HWE olefination and in situ chemoselective olefin saturation were achieved to provide saturated esters **11** (Scheme 6). We conjectured that Ir catalyst and hydrosilane (not dihydrosilane, which can allow ester hydrosilylation) can effect chemoselective saturation of enoates.[19] When triethylsilane was added to the reaction mixture from HWE reaction of esters **4**, which was warmed to 80 °C in a closed vessel, we observed chemoselective olefin reduction to afford two-carbon-homologated saturated esters **11a−e**.

Scheme 6. In Situ Olefin Saturation



The HWE reaction, using sodium hydride as a base, of TBS-protected Roche aldehyde led to partial epimerization.[20] We further investigated whether the stereogenic center of the ester would be epimerized under our reaction conditions coupled with Ando's *Z*-selective HWE reaction.[21] When TBS-protected (*R*)-(−)-Roche ester **13** was subjected to these reaction conditions, erosion of enantioselectivity in **14** was not observed (Scheme 7).

Scheme 7. *Z*-Selective Ir-Catalyzed Reductive HWE of (*R*)-(−)-Roche Ester



In summary, an operationally convenient, single-pot, catalytic reductive HWE olefination was developed. The strategy is based on Lewis base promoted deprotonative pronucleophile addition to silyl acetals. This sequential reaction proceeds at rt and does not require premetalation of phosphonates. Notably, traditionally difficult ester substrates bearing aryl, alkenyl, and alkynyl moieties converted to the corresponding cinnamates, dienoates, and ynenoates with excellent stereoselectivities and good to excellent yields. Finally, we demonstrated single-pot Ir-catalyzed reductive HWE olefination and in situ chemoselective olefin saturation to directly provide two-carbon-homologated saturated esters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02901.

Spectroscopic characterization data and procedures for preparation of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(14) Heteroatom-bonded acyclic hydridobisimidazolium pentacoordinate silicate salts {i.e., [Nu$_2^{2+}$Si$^-$Me$_2$H]X$^-$ (Nu = 3-methyl-1-imidazolio, *N*,*N*-dimethylaminopyridinio, pyridinio; X = Cl, I, OSO$_2$CF$_3$)} were characterized via ^{28}Si NMR spectroscopy.

(15) Hydrosilylation of differently substituted esters has been studied. (a) See ref 11. (b) Hua, Y.; Asgari, P.; Dakarapu, U. S.; Jeon, J. *Chem. Commun.* **2015**, *51*, 3778−3781. (c) Hua, Y.; Jung, S.; Roh, J.; Jeon, J. *J. Org. Chem.* **2015**, *80*, 4661−4671.

(16) Formation of the methyl ester via *trans*-esterification (<3%) and saturated byproduct (<1%) was observed over an extended period of reaction time.

(17) When **3a** was treated with KOSiMe$_3$ in the absence of external reducing agents (e.g., diethylsilane) and pronucleophile (e.g., trimethyl phosphonoacetate), a carbonyl hydrosilylation adduct (99%) was exclusively produced. One possible explanation is that the fully dissociated aldehyde **8a** reacts with disiloxane **7** (R^3 = Et). However, during our studies on the reductive HWE olefination, we did not observe the formation of the hydrosilylation adduct. (a) Sonnek, G.; Drahs, E.; Jancke, H.; Hamann, H. *J. Organomet. Chem.* **1990**, *386*, 29−35. (b) Chuit, C.; Corriu, R. J. P.; Perz, R.; Reye, C. *Synthesis* **1982**, *1982*, 981−984. (c) Schiffers, R.; Kagan, H. B. *Synlett* **1997**, *1997*, 1175. (d) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443−444.

(18) General procedure: (i) [Ir(coe)$_2$Cl]$_2$ (0.9 mg, 0.1 mol %) and **4** (1 mmol) were added to a flame-dried, nitrogen-purged septum-capped vial. The mixture was dissolved with CH$_2$Cl$_2$ (0.30 mL, 3.3 M), and H$_2$SiEt$_2$ (0.26 mL, 2 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner under a N$_2$ atmosphere [note: diethylsilane (bp 56 °C and density 0.686 g/mL) is volatile]. The reaction mixture was stirred at rt for 8 h. Volatiles were removed in vacuo to afford the diethylhydrosilyl acetals, which were directly used for subsequent reactions without further purification. (ii) Crude silyl acetals were dissolved in THF (6.30 mL, 0.16 M), and alkyl phosphonoacetate (1.1 mmol) and KOSiMe$_3$ (128.3 mg, 1 mmol) in THF (6.30 mL, 0.16 M) were added at rt [in the instance of aliphatic enoate-derived silyl acetals, KOSiMe$_3$ was added at 0 °C]. After being stirred for 30 min, the reaction mixture was quenched with saturated aq NH$_4$Cl and extracted with diethyl ether. The combined organic extracts were washed with brine and dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by MPLC to afford the corresponding enoates **5**.

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