JOC*Note*

Synthesis of 1,2-Diketones by the Transition Metal-Catalyst-Free Reaction of α-Oxo Acid Chlorides or Oxalyl Chloride with Organostannanes

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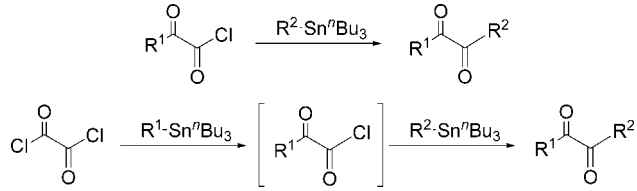
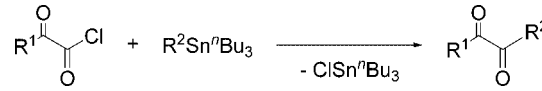


The reaction of an α-oxo acid chloride with an organostannane proceeds transition metal-catalyst-free to afford a 1,2-diketone in an excellent yield. In addition, a sequence comprising pretreatment of oxalyl chloride with an organostannane and a subsequent treatment with another organostannane also works as a convenient modification.

Electrophilic substitution at an aryl−Sn bond is a well-known process.[1] For instance, the $AlCl_3$-catalyzed reaction of arylstannanes with acid chlorides affords aryl ketones in high yields.[2] Ketone synthesis by transition metal-catalyzed cross-coupling of acid chlorides with organostannanes is also well studied since the pioneering work by Kosugi−Migita[3] and also that by Stille−Milstein.[4] The Stille−Milstein procedure using a palladium complex catalyst was also applied to the synthesis of 1,2-diketones starting with acyl chlorides and acylstannane reagents, although the reaction required long heating at high temperatures, resulting in only moderate yields.[5] On the other hand, one of us reported near-quantitative synthesis of α-oxo nitriles[6] and α-oxo amides[7] by the reactions of Bu_3Sn-CN and Me_3Sn-CON^iPr_2 with acid chloride derivatives, which work

SCHEME 1. Transition Metal-Catalyst-Free 1,2-Diketone Synthesis Starting with α-Oxo Acid Chloride and Organostannane



catalyst-free under much milder reaction conditions (rt ∼75 °C, less than 1 h in most cases). Besides these, when the Sn−C bond is somehow activated by an α-heteroatom, the cross-coupling appears to proceed catalyst-free. Thus, the reaction with (α-sulfonylcyclopropyl)stannane and (α-sulfonylvinyl)-stannane reagents affords corresponding α-sulfonylcyclopropy and α-sulfonylvinyl ketones in fair to high yields.[8] α-Stannylpyridines and α-stannylpyrimidines are also reactive under catalyst-free and exceptionally mild conditions toward acyl chlorides to furnish corresponding heterocyclic ketones.[9] However, similar reactions of α-oxo acyl chlorides with α-stannylpyridines and α-stannylpyrimidines do not afford diketones selectively, but also form the "mono" ketones, due to concomitant decarbonylation, which is believed to stem from the participation of α-nitrogen. The only catalyst-free cross-coupling of simple organostannane compounds appeared quite recently and disclosed the necessity of harsh conditions (130 °C, up to 90 h) and only moderate yields being obtained.[10]

During the course of our research on the transition metal-catalyzed reactions of α-oxo acid chlorides, we have come accidentally across high-yielding formation of 1,2-diketones in the reaction with organostannane compounds in the absence of a transition metal catalyst (Scheme 1), which will be disclosed in this note. There are quite a few synthetic methodologies for simple 1,2-diketones (vide infra),[11] but synthesis of alkenyl and alkynyl 1,2-diketones has been very limited.[12]

In a representative experiment, a toluene solution of phenyl-2-oxoacetyl chloride **1a** and tri-*n*-butyl(allyl)stannane **2A** was stirred at 110 °C for 3 h. Routine workup of the resulting mixture, inclusive of treatment with aqueous potassium fluoride to convert chlorotri-*n*-butylstannane coproduct to an insoluble polymeric material, followed by preparative TLC afforded 1-phenylpent-4-ene-1,2-dione **3aA** in 96% isolated yield. The product showed satisfactory spectral data.

Interestingly, when a trial reaction of **1a** with **2A** (1 equiv) was run, according to the Migita−Kosugi procedure with $RhCl(PPh_3)_3$ (2.0 mol %) at 80 °C for 3 h, the desired diketone was not formed in an appreciable yield, and instead, 1-phenyl-

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but-3-en-1-one (11%) and 1-phenylbut-2-en-1-one (7%; the *E*/*Z* ratio was ca. 2/1) were formed.[13] Likewise, another $RhCl(PPh_3)_3$-catalyzed reaction (80 °C for 5 h) of **1a** with (phenylethynyl)tri-*n*-butylstannane **2D**, which is one of the most reactive stannane reagents in transmetalation chemistry,[14] also failed to give the desired 1,4-diphenylbut-3-yne-1,2-dione, ending up with the formation of diphenylacetylene (5%) and 1,4-diphenylbutadiyne (34%). In contrast to these, a control experiment with **1a** and **2A** run in the absence of the catalyst at 80 °C for 3 h afforded the desired diketone **3aA** in 54% yield. These experiments indicate that the rhodium complex promotes the reaction rapidly, but in an undesired direction.

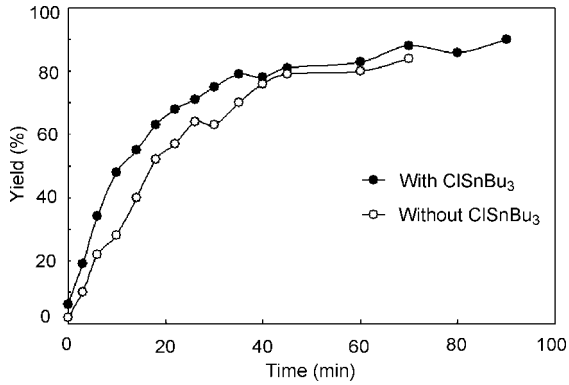
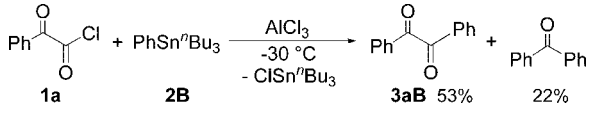


FIGURE 1. Time-course of the reaction of **1b** with **2B** in the absence (○) or presence (●) of chlorotri-*n*-butylstannane monitored by ^1H NMR spectroscopy.

Another aspect that merits consideration is the possible role of the coproduced chlorotri-*n*-butylstannane as a Lewis acid catalyst. The time-course of the reaction of *p*-anisyl-2-oxoacetyl chloride **1b** and phenyltri-*n*-butylstannane **2B** (1 equiv) run at 80 °C in toluene-d_8 did not display a clear sigmoidal increase of the yield of 1-(*p*-anisyl)-2-phenylethanedione **3bB**, which should have been seen in an autocatalytic reaction (Figure 1). However, the same reaction run in the presence of a catalytic quantity of chlorotri-*n*-butylstannane (10 mol %) was distinctly faster, in particular in the early stages, suggesting that chlorotri-*n*-butylstannane does work as a catalyst, albeit weakly.

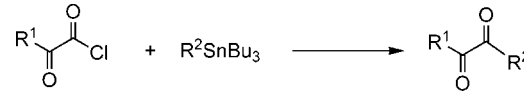
SCHEME 2. Aluminum Chloride-Catalyzed Reaction of Phenyl-2-oxoacetyl Chloride with Phenyltri-*n*-butylstannane



To gain a rough estimate of the catalytic activity of chlorotri-*n*-butylstannane relative to trichloroaluminum, we ran a reaction of phenyl-2-oxoacetyl chloride **1a** with phenyltri-*n*-butylstannane **2B** (1 equiv) in the presence of trichloroaluminum (10 mol %) in dichloromethane (2 mL) at −30 °C for 3 h (Scheme 2). Analysis of the mixture by GC revealed the formation of benzil **3aB** in 53% along with benzophenone (22%). The result indicates that trichloroaluminum promotes the reaction as a powerful Lewis acid even at a low temperature, but the benzophenone formation via decarbonylation is a serious drawback.

The new methodology described in the representative experiment appears quite general, irrespective of the structure of α-oxo acid chlorides and organostannane compounds as summarized in Table 1. Thus, besides the allylstannane **2A** already mentioned, phenyl-, vinyl-, ethynyl-, and benzylstannanes **2B**−**E** all reacted smoothly with **1a**, affording near-quantitative yields of corresponding 1,2-diketones. More amazing is that even tetra-*n*-butylstannane **2F**, which is envisioned to be least reactive in electrophilic substitution,[1b,14] does react without any difficulty, ending up with a near-quantitative yield. Since the reactivity of phenyltri-*n*-butylstannane **2B** is so high, the substituent-dependent difference in reactivity is not evident as far as substituted phenyl-2-oxoacetyl chlorides **1b**−**d** are concerned. The reaction of heteroaromatic (**1e**) and aliphatic (**1f**) α-oxo acid chlorides also proceeds as well, thus proving that the reaction offers a straightforward and general methodology for the synthesis of various 1,2-diketones. Note that, although the reaction listed in Table 1 was run for 3 h, a long duration of the reaction may not be required, depending on the combination of **1** and **2**, as the time-course experiment with **1b** and **2B** (vide supra) suggests.

TABLE 1. Reaction of α-Oxo Acid Chloride 1 with Organostannane 2[a]



entry	**1**, R^2 =	**2**, R^2 =	product, yield (%)[b]
1	**1a**, Ph	**2A**, allyl	**3aA**, (96)
2	**1a**	**2B**, Ph	**3aB**, 99[c] (95)
3	**1a**	**2C**, vinyl	**3aC**, quant
4	**1a**	**2D**, phenylethynyl	**3aD**, quant (93)
5	**1a**	**2E**, benzyl	**3aE**, 88
6	**1a**	**2F**, *n*-Bu	**3aF**, 98
7	**1b**, *p*-$MeOC_6H_4$	**2B**	**3bB**, quant
8	**1c**, *p*-ClC6H$_4$	**2B**	**3cB**, 97
9	**1d**, C_6F_5	**2B**	**3dB**, 98[d]
10	**1e**, 2-thienyl	**2B**	**3eB**, quant
11	**1f**, Me	**2B**	**3fB**, 97[c]

[a] Reaction conditions: a mixture of **1** (0.5 mmol), **2** (0.5 mmol), and toluene (3 mL) was stirred for 3 h at 110 °C. [b] Determined by ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The numbers in parentheses are isolated yields. [c] Determined by GC with *n*-tetradecane as an internal standard. [d] Determined by ^{19}F NMR spectroscopy with hexafluorobenzene as an internal standard.

We have also attempted the reaction of **1a** with (trimethylsilyl)tri-*n*-butylstannane (100 °C, 3 h), aiming at the synthesis of either 1-phenyl-2-(trimethylsilyl)ethane-1,2-dione or 1-phenyl-2-(tri-*n*-butylstannyl)ethane-1,2-dione.[15,16] However, none of these were formed at all and both starting materials remained unchanged. Likewise the reaction with hexa-*n*-butyldistannane did not form stannyl diketone either, although a trace of chlorotri-*n*-butylstannane was detected in the resulting mixture.

(13) Other unidentified byproducts were also formed. Although Kosugi and co-workers reported higher yields for the $RhCl(PPh_3)_3$-catalyzed reaction (40 °C) of simple acid chlorides with **2A**, use of a large excess of acid chlorides appears prerequisite for the high yield, which may be associated with the decarbonylation of acid chlorides. See ref 3.

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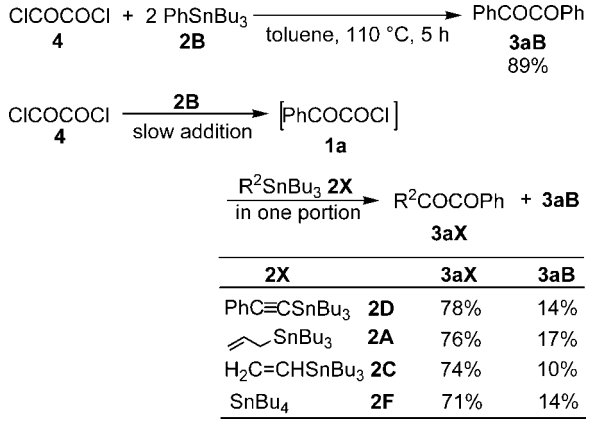
(16) In transmetalation between (trimethylsilyl)tri-*n*-butylstannane (Si-Sn) and an organopalladiumhalide complex (R-Pd-X), formation of both R-Pd-Si and R-Pd-Sn appears possible, depending on the particular structure of the complex. See: (a) Mori, M.; Kaneta, N.; Shibasaki, M. *J. Org. Chem.* **1991**, *56*, 3486. (b) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1995**, *117*, 9814.

SCHEME 3. 1,2-Diketone Synthesis Starting with Oxalyl Chloride



2X		3aX	3aB
PhC≡CSnBu$_3$	**2D**	78%	14%
SnBu$_3$	**2A**	76%	17%
H$_2$C=CHSnBu$_3$	**2C**	74%	10%
SnBu$_4$	**2F**	71%	14%

Encouraged by the high-yielding synthesis of 1,2-diketones, we assumed that oxalyl chloride **4** could form 1,2-diketone when treated with organostannanes, which indeed turned out to be a convenient modification in two directions. One is the synthesis of symmetrical diketone, as exemplified by the synthesis of benzil as shown in Scheme 3 (top). Heating a toluene solution of **4** and 2 equiv of phenyltri-*n*-butylstannane **2B** at 110 °C for 5 h gave benzil **3aB** in 89% GC yield. In the other (Scheme 3, bottom), to a toluene solution of **4** was added a toluene solution of phenyltri-*n*-butylstannane **2B** (1 equiv) at 60 °C, slowly by using a syringe pump. After heating for another 2 h, (phenylethynyl)tri-*n*-butylstannane **2D** (1 equiv) in toluene was added in one portion to the resulting mixture and the mixture was further heated for 3 h. GC analysis revealed the formation of 1,4-diphenylbut-3-yne-1,2-dione **3aD** (78% GC yield) along with benzil **3aB** (14% GC yield). Similar reactions with allyltri-*n*-butylstannane **2A**, vinyltri-*n*-butylstannane **2C**, and tetra-*n*-butylstannane **2F** in place of **2D** also furnished corresponding 1,2-diketones (**3aA**, **3aC**, and **3aF**) in 71−76% yields, together with benzil **3aB**. These reactions suggest that α-oxo acid chlorides **1**, synthesis of which occasionally requires tedious multistep processes, including the preparation of α-oxo acids[17] and subsequent chlorination,[18] using toxic reagents, can be generated rather cleanly. To substantiate the suggestion, a toluene solution of phenyltri-*n*-butylstannane **2B** was added at 70 °C slowly over a period of 2 h by using a syringe pump to a toluene (5 mL) solution of oxalyl chloride **4** (1 equiv) and the mixture was heated for another 2 h. Analysis by GC revealed the formation of phenyl-2-oxoacetyl chloride **1a** in 76% yield. This in situ generation of α-oxo acid chloride is also of great synthetic value in its own right.

To summarize we have developed a transition metal-catalyst-free coupling of α-oxo acyl chlorides with organostannanes, which serves as a general, simple, and high-yielding methodology to synthesize 1,2-diketones. An easy synthesis of α-oxo acyl chlorides has also been made possible via coupling of oxalyl chlorides with organostannanes. 1,2-Diketones are useful as medicinally active compounds.[19] They are also versatile intermediates in synthetic applications, for instance, the synthesis of heterocyclic compounds[20] and ligands for inorganic complexes.[21] Accordingly, synthesis of 1,2-diketones has been a subject of extensive research and numerous methodologies have been proposed,[11] mainly by oxidation of ketones or α-functionalized ketones,[12,22e] 1,2-diols,[12f,23] alkynes,[20g,24] olefins,[25] epoxides,[26] and 1,2-dihalides[27] and also by other miscellaneous methods.[28] We envision that the new findings herein reported will find broad utility in organic synthesis.

Experimental Section

Typical Procedure for the Reaction of α-Oxo Acid Chlorides with Organostannanes: The Reaction of Phenyl-2-oxoacetyl Chloride (1a) with Allyltri-*n*-butylstannane (2A). A mixture of phenyl-2-oxoacetyl chloride **1a** (85 mg, 0.51 mmol) and allyl(tri-*n*-butyl)stannane (**2A**, 0.15 mL, 0.48 mmol) in toluene (4 mL) was heated for 3 h at 110 °C. After cooling to room temperature, the mixture was analyzed by ^{1}H NMR spectroscopy by using 1,1,2,2-tetrachloroethane (9.2 mg) added as an internal standard. Then the reaction mixture was diluted with methyl *tert*-butyl ether (10 mL) and a 5 mL portion of a saturated aqueous KF solution (ca. 10 wt %) was added. The organic layer was separated from the resulting suspension. Another 5 mL portion of the KF solution was added and the mixture was processed similarly. The organic layer separated from the second KF treatment was dried over Na_2SO_4, filtered, and evaporated. The residue was subjected to preparative TLC (silica gel, hexane/acetone = 85/15) to give 1-phenylpent-4-

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ene-1,2-dione **3aA** (81 mg, 0.46 mmol, 96% isolated yield) as pale yellow oil. ^{1}H NMR δ 7.99 (dd, J = 1.07, 8.3 Hz, 2H, *o*-Ph), 7.65 (t, J = 7.1 Hz, 1H, *p*-Ph), 7.54−7.39 (m, 3H, *m*-Ph and H*H*C═CH, overlapped), 7.01 (ddt, $^3J_{HH\text{-}trans}$ = 16.0 Hz, $^3J_{HH}$ = 6.8, $^3J_{HH\text{-}cis}$ = 10.1 Hz, 1H, HHC═C*H*), 6.48 (dd, $^3J_{HH}$ = 1.5 Hz, $^3J_{HH\text{-}trans}$ = 16.0 Hz, 1H, *H*HC═CH), 2.02 (d, $^3J_{HH}$ = 6.8 Hz, 2H, $COCH_2$); ^{13}C{^{1}H} NMR δ 194.2 (CO), 194.0 (CO), 151.5 (COCC*C*), 135.0 (COC*C*C), 133.1 (*ipso*-Ph), 130.4 (*o*-Ph), 129.2 (*m*-Ph), 129.0 (*p*-Ph), 19.6 (CO*C*CC); IR (neat, cm^{-1}) 1674 (br, ν_{CO}), 1624 ($\nu_{C=C}$); GCMS (70 eV) *m*/*z* (% rel intensity) 174 (12, [M]$^+$), 105 (100), 77 (12), 69 (21); HRMS (EI) calcd for $C_{11}H_{10}O_2$ 174.0681, found 174.0684. For ^{1}H and ^{13}C NMR spectra, see appendices 3 and 4 in the Supporting Information.

Reaction of Oxalyl Chloride with Phenyltri-*n*-butylstannane. To oxalyl chloride (63.0 mg, 0.496 mmol) and toluene (3 mL) placed in a 20 mL Schlenk tube was added phenyltri-*n*-butylstannane (368 mg, 1.00 mmol) and the mixture was heated at 110 °C for 5 h. GC analysis with tetradecane (6.3 mg) as internal standard revealed the formation of benzil in 89% yield.

Synthesis of 1,2-Diphenylbut-3-yne-1,2-dione (3aD) by the Reaction of Oxalyl Chloride with Phenyltri-*n*-butylstannane Followed by (Phenylethynyl)tri-*n*-butylstannane. At 60 °C, to oxalyl chloride (62.8 mg, 0.498 mmol) and toluene (5 mL) placed in a 20 mL Schlenk tube was added a solution of phenyltri-*n*-butylstannane (185 mg, 0.504 mmol) in toluene (2 mL) slowly over a period of 2 h by using a syringe pump and the mixture was heated for another 2 h at that temperature. Subsequently, (phenylethynyl)tri-*n*-butylstannane (199 mg, 0.509 mmol) was added in one portion and the mixture was heated for an additional 3 h. GC analysis with tetradecane (11.3 mg) as internal standard revealed the formation of **3aD** in 78% yield along with benzil in 14% yield.

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Supporting Information Available: Experimental details and spectral data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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