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One-Pot Synthesis of (*E*)-Styryl Ketones from Styrenes

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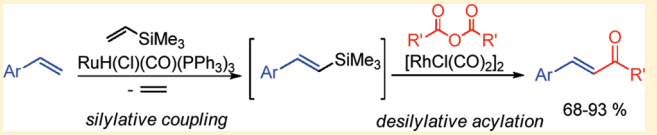
Supporting Information

ABSTRACT: A new, efficient protocol for the highly stereoselective one-pot synthesis of (*E*)-styryl ketones from styrenes based on sequential ruthenium-catalyzed silylative coupling—rhodium-catalyzed desilylative acylation reactions is reported.



α,β-Unsaturated ketones have been widely applied as useful key reagents in organic synthesis.[1] Their use as substrates for a number of reactions such as Michael addition,[1] hydrogenation,[2] epoxidation,[3] cycloaddition,[4] Morita—Baylis—Hillman reaction,[5] etc., has stimulated their synthetic advancements.

The most common access to (*E*)-α,β-unsaturated ketones is by the Claisen—Schmidt condensation of aldehydes and ketones under basic conditions.[6] However, this method suffers from the drawbacks of narrow substrate diversity, the reversibility of the aldol addition, and side reactions such as isomerization, ketone self-condensation, and Michael addition. An elegant solution to these problems is a Mukaiyama aldol reaction followed by subsequent dehydration catalyzed by a Lewis acid[7] or catalytic aldol condensation between alkenyl trichloroacetates and aldehydes reported by Yanagisawa et al.[8] Alternatively, stereodefined α,β-unsaturated ketones may be formed by selective oxidation of allylic alcohols[9] or Friedel—Crafts acylation of arenes by α,β-unsaturated acyl chlorides.[10]

In addition, a number of transition-metal-catalyzed methodologies for the preparation of (*E*)-α,β-unsaturated ketones have been developed over the last two decades. α,β-Unsaturated ketones may be formed by the selective ruthenium-catalyzed cross-metathesis of vinyl ketones with terminal alkenes[11] or rhodium-catalyzed carbonylative addition of arylboronic acids to terminal alkynes.[12] Palladium-catalyzed Heck-type coupling of vinyl ketone derivatives with iodoarenes[13] or aryl boronic acids[14] are also valuable C—C bond-forming reactions, which allow the formation of α,β-unsaturated ketones; however, the poor availability and stability of vinyl ketones and the competitive conjugate addition reaction limit their use. A new catalytic approach based on palladium-catalyzed carbonylative Heck reaction of aryl halides or aryl triflates and styrenes has been also recently reported by Beller and co-workers.[15]

In the past two decades, we have developed the silylative coupling of olefins with vinyl-substituted organosilicon compounds occurring in the presence of complexes containing initially or generating in situ M—H and M—Si bonds.[16] The mechanism of the process proposed for the Ru complexes proceeds via insertion of vinylsilane into Ru—H bond and β-Si transfer to the metal with elimination of ethylene to generate Ru—Si species, followed by insertion of alkene and β-H transfer to the metal with elimination of the substituted vinylsilane (Scheme 1).[16]

The silylative coupling, in combination with subsequent desilylation reactions such as Hiyama cross-coupling and halodesilylation appears to be a valuable step to provide functionalized unsaturated organic compounds such as (*E*)-stilbenes, aryl-substituted polyenes, or (*E*)-styryl halides.[17]

On the other hand, acylation of stereodefined vinylsilanes by acid halides in the presence of Lewis acids proceeds in a regioselective manner to afford α,β-unsaturated ketones.[18] Recently, Narasaka and co-workers developed a catalytic acylation of vinylsilanes with acid anhydrides by the use of a rhodium complex which avoids the use of large quantities of strong Lewis acids and highly reactive and harmful acid halides.[19] The mechanism of the catalytic acylation proceeds via transmetalation between the Rh(I) complex and vinylsilane to afford vinylrhodium intermediate, followed by sequential oxidative addition of acid anhydride and reductive elimination of α,β-unsaturated ketone with regeneration of Rh(I) catalyst (Scheme 2).[19a]

The sequential Hiyama cross-coupling/Narasaka acylation reactions have been also successfully applied to the synthesis of α,β-unsaturated carbonyl motifs.[20] This catalytic acylation protocol has been developed mostly for dimethylphenyl-substituted vinylsilanes, which appears to be more reactive than vinylsilanes with trimethylsilyl groups under the given conditions (1,4-dioxane, 90 °C). However, in spite of the availability and stability of the unsaturated trimethylsilyl derivatives, the development of the conditions for their selective conversion to stereodefined α,β-unsaturated ketones is of significance.

We have envisaged that the ruthenium-catalyzed *E*-selective silylative coupling of styrenes with trimethylvinylsilane followed by rhodium-catalyzed acylation can be a valuable and complementary synthetic method for one-pot conversion of styrenes into (*E*)-styryl ketones (Scheme 3). Therefore, in this paper, we report a facile one-pot preparation of (*E*)-styryl ketones from

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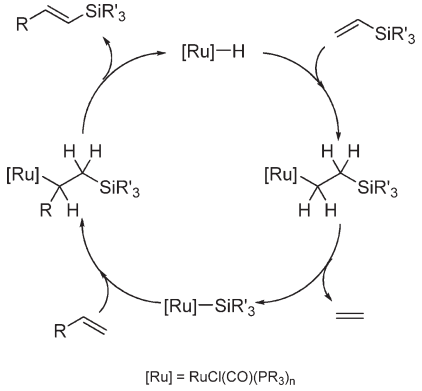
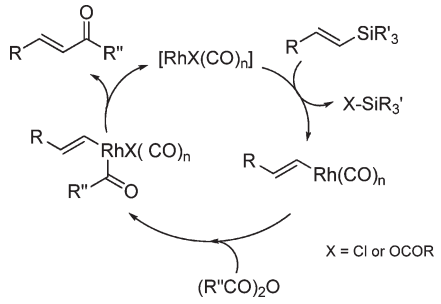
Scheme 1. Silylative Coupling Mechanism



Scheme 2. Mechanism of the Rhodium-Catalyzed Acylation of Vinylsilanes

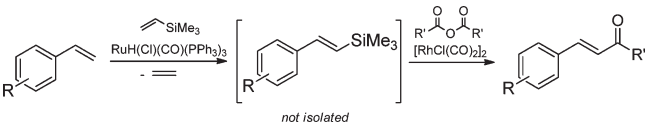


styrenes via the corresponding (*E*)-styryltrimethylsilane intermediates.

As we have previously reported, the silylative coupling of substituted styrenes with vinylsilanes catalyzed by ruthenium—hydride or ruthenium—silyl complexes occurred stereoselectively to give (*E*)-*β*-silylstyrenes in high yields.[21] For preliminary results on the silylative coupling reaction, equimolar amounts of the commercially available 4-chlorostyrene and trimethylvinylsilane were used, and the reaction was conducted following the original procedure ($RuHCl(CO)(PPh_3)_3$ catalyst (1 mol %) toluene, 6 h, 100 °C, sealed ampule)[21a] to give exclusively (*E*)-4-chlorostyryltrimethylsilane (GC yield 98%). Treatment of the isolated (*E*)-4-chlorostyryltrimethylsilane with 3 equiv of acetic anhydride in the presence of rhodium catalyst $[RhCl(CO)_2]_2$ (5 mol %) in dry 1,4-dioxane at 90 °C for 24 h under Ar atmosphere according to the method described by Narasaka and co-workers[19] allowed isolation of stereochemically pure (*E*)-4-chlorostyryl methyl ketone in 70% yield. Thus, by sequencing the highly *E*-selective silylative coupling of 4-chlorostyrene with a stereospecific acylation, the stereochemical fidelity of the product is preserved.

Since a single example of the efficient acylation of (*E*)-dimethylphenyl(4-phenylbut-1-en-1-yl)silane by acetic anhydride in toluene has been reported by Narasaka and co-workers,[19b] we tested this solvent for the desilylative acylation of styrylsilanes. After several attempts, we found that acylation of (*E*)-4-chlorostyryltrimethylsilane by acetic anhydride in the presence of rhodium catalyst in dry toluene occurs more efficiently (95% GC yield) at higher temperature (120 °C) in a closed reaction vessel without affecting the stereoselectivity of the process.

Scheme 3. Proposed Synthesis of (*E*)-Styryl Ketones



Since both reactions, i.e., silylative coupling and desilylative acylation, can be performed in toluene, this result prompted us to attempt the acylation step in one pot with silylative coupling without further purification of the (*E*)-styrylsilane intermediate. In a typical procedure, 4-chlorostyrene, trimethylvinylsilane (1:1 ratio), and $RuHCl(CO)(PPh_3)_3$ catalyst (1 mol %) were dissolved in toluene (0.5 M concentration) and heated in a Schlenk bomb flask fitted with a plug valve at 100 °C for 6 h under Ar atmosphere. Next, after the reaction was cooled to room temperature, 3 equiv of acetyl anhydride and 5 mol % of solid $[RhCl(CO)_2]_2$ were added, and the reaction mixture was heated to 120 °C. Treatment of the silylative coupling product with anhydride caused acylation in a stereospecific manner giving (*E*)-4-chlorostyryl methyl ketone in high geometrical purity (*E*/*Z* = 99/1) within 18 h. Column chromatography of the resulting product (silica gel, eluent: hexane/diethyl ether 8:2) afforded pure (*E*)-4-chlorostyryl methyl ketone **1** in 90% overall yield (entry 1, Table 1).

Given our optimized conditions, we investigated the scope of this one-pot reaction sequence using various substituted styrenes and selected carboxylic acid anhydrides (Table 1). Since the synthetic procedure requires the absence of byproducts of the *homo*-coupling of trimethylvinylsilane—1,2-bis(trimethylsilyl)-ethenes which could form diketone side products, all the silylative coupling reactions were performed at the 1:1 ratio of substrates. Moreover, the silylative coupling reactions were carried out in a 0.5 M solution of toluene to minimize polymerization of styrenes. Under these conditions, substituted styrenes bearing functional groups such as —Me, —OMe, —Cl, and —Br reacted successfully to give the corresponding (*E*)-styryl ketones in high yields, irrespective of the substituent's electronic character and position in the aromatic ring (Table 1). Both saturated and unsaturated acid anhydrides can be employed for the acylation of (*E*)-styrylsilanes to give corresponding (*E*)-styryl ketones with moderate to high yields. However, when butyric and benzoic anhydride were applied as the acylating agents (Table 1, entries 4—7), the reaction required a longer time (40—48 h). Moreover, in the reactions with benzoic anhydride, z excellent. In all cases, the *E*-double bond geometry was strongly favored, with approximately 99:1 *E*/*Z* ratio as measured by ^1H NMR.

Efforts were made to further improve the procedure by examining tandem catalysis using one catalyst for both silylative coupling and acylation steps. Unfortunately, the silylative coupling of styrenes with vinyltrimethylsilane in the presence of $[RhCl(CO)_2]_2$ was unsuccessful. Other rhodium precursors which are known to be active in the silylative coupling reaction,[23] e.g., $[RhCl(cod)]_2$, $[Rh(OSiMe_3)(cod)]_2$, and $RhH(CO)(PPh_3)_3$, also failed as potential Narasaka acylation catalysts.

In summary, we have devised a new versatile one-pot protocol for stereoselective preparation of (*E*)-styryl ketones via a highly selective catalytic silylative coupling/desilylative acylation sequence. Starting from easily available and inexpensive styrenes, vinylsilane, and carboxylic acid anhydrides the corresponding

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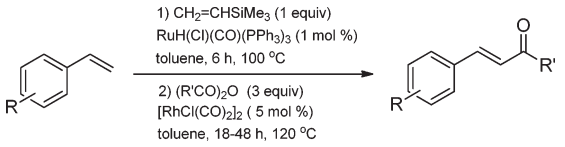
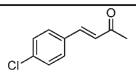
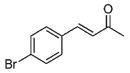
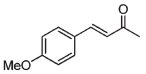
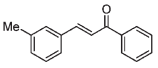
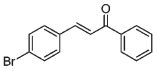
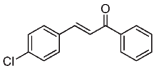
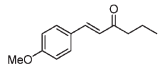
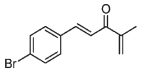
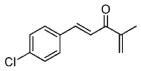
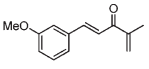
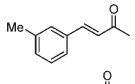
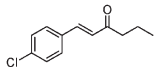
Table 1. One-Pot Synthesis of (*E*)-Styryl Ketones from Styrenes



Entry	R	R'	Product structure		Time [h]	Yield (%)[a]
1	4-Cl	Me		**1**	18	90
2	4-Br	Me		**2**	20	93
3	4-MeO	Me		**3**	24	80
4	3-Me	Ph		**4**	40	79
5	4-Br	Ph		**5**	45	83
6	4-Cl	Ph		**6**	40	70
7	4-MeO	Pr		**7**	48	72
8	4-Br	-C(Me)=CH$_2$		**8**	24	72
9	4-Cl	-C(Me)=CH$_2$		**9**	24	74
10	3-MeO	-C(Me)=CH$_2$		**10**	24	68
11	3-Me	Me			24	79[b]
12	4-Cl	Pr			40	90[b]

[a] Overall yield of isolated products. [b] GC yield.

unsaturated ketones are obtained in generally good yields and selectivities.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of (*E*)-Styryl Ketones. A mixture consisting of 5 mmol of substituted styrene, 0.5 g (5 mmol) of vinyltrimethylsilane, 47.6 mg (0.05 mmol) of $RuHCl(CO)(PPh_3)_3$, and 10 mL of dry toluene was placed under Ar atmosphere in a Schlenk bomb flask fitted with a plug valve and heated at 100 °C for 6 h. After the reaction was completed (GC analysis), 0.25 mmol (97.20 mg) of $[RhCl(CO)_2]_2$ and 15 mmol of anhydride were added. The mixture was stirred for 24−48 h (see Table 1) at 120 °C. After this time the solvent was evaporated and the crude product was purified by column chromatography on silica gel, eluting with *n*-hexane/diethyl ether in a ratio of 8:2 to give the corresponding ketone.

(*E*)-4-(4-Chlorophenyl)but-3-en-2-one[24] (1). Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H,), 6.65 (d, 1H, J = 16.3 Hz), 7.29−7.43 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.7, 127.4, 129.2, 129.4, 132.9, 136.4, 141.8, 198.1. MS m/z (rel int): 180 (M^+, 30), 165 (100), 145 (52), 137 (60), 102 (77), 75 (43), 50 (30). HRMS calcd for $C_{10}H_9ClO$: 180.03419, found 180.03370.

(*E*)-4-(4-Bromophenyl)but-3-en-2-one[24] (2). Yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 6.70 (d, 1H, J = 16.3 Hz), 7.38−7.55 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.7, 127.5, 124.7, 129.3, 129.4, 132.2, 141.9, 198.1. MS m/z (rel int): 226 (M^+ 30), 211 (54), 183 (30), 145 (75), 130 (22), 102 (100), 75 (25), 50 (30). HRMS calcd for $C_{10}H_9BrO$: 223.98368, found 223.98297.

(*E*)-4-(4-methoxyphenyl)but-3-en-2-one[24] (3). Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 3.84 (s, 3H), 6.61 (d, 1H, J = 16.2 Hz), 6.91−6.34 (m, 2H), 7.45−7.52 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9, 55.4, 114.4, 125.0, 127.1, 161.6, 129.6, 143.3, 206.9. MS m/z (rel int): 176 (M^+, 42), 161 (100), 145 (20), 133 (52), 118 (25), 89 (21), 77 (22), 63 (20). HRMS calcd for $C_{11}H_{12}O_2$: 176.08373, found 176.08310.

(*E*)-1-Phenyl-3-(3-tolyl)prop-2-en-1-one[25] (4). Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (d, 3H), 7.14−7.34 (m, 3H), 7.36−7.54 (m, 5H), 7.72 (d, 1H, J = 15.7 Hz), 7.94−7.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 125.7, 128.5, 128.6, 128.8, 129.1, 131.4, 132.7, 134.8, 138.3, 138.6, 121.8, 145.1, 190.6. MS m/z (rel int): 221 (M^+, 45), 207 (100), 180 (15), 145 (15), 115 (30), 89 (21), 77 (25), 20 (20). HRMS calcd for $C_{16}H_{14}O$: 222.10447, found 222.10310.

(*E*)-3-(4-Bromophenyl)-1-phenylprop-2-en-1-one[26] (5). Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49−7.62 (m, 8H), 7.75 (d, 1H, J = 15.8 Hz), 8.04 (dd, 2H, J = 8.2, 1.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.5, 128.5, 128.7, 129.2, 129.8, 130.2, 132.2, 133.0, 133.8, 143.4, 190.2. MS m/z (rel int): 286 (M^+, 60), 207 (100), 179 (50), 178 (35), 130 (32), 105 (33), 102 (85), 77 (87), 51 (55). HRMS calcd for $C_{15}H_{11}BrO$: 285.99933, found 285.99725.

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one[26] (6). Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, 2H, J = 8.4 Hz), 7.47−7.60 (m, 6H), 7.65−7.79 (m, 1H), 8.00−8.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.4, 128.5, 128.7, 128.9, 129.2, 129.6, 130.5, 132.9, 134.5, 143.3, 190.4. MS m/z (rel int): 242 (M^+, 80), 208 (75), 179 (50), 165 (45), 130 (25), 102 (50), 77 (100), 51 (70). HRMS calcd for $C_{15}H_{11}ClO$: 242.04984, found 242.04932.

(*E*)-1-(4-Methoxyphenyl)hex-1-en-3-one[24] (7). Yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95−1.00 (t, 3H, J = 7.3 Hz), 1.58−1.74 (m, 2H), 2.60−2.65 (t, 2H, J = 7.2 Hz), 3.84 (s, 3H), 6.63 (d, 1H, J = 16.2 Hz), 6.89−6.93 (m, 2H), 7.49−7.54 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 17.9, 42.7, 55.4, 114.4, 124.2, 127.2, 161.5, 129.9, 142.1, 200.6. MS m/z (rel int): 204 (M^+, 30), 161 (60), 133 (26), 118 (10), 89 (12), 77 (12), 63 (13). HRMS calcd for $C_{13}H_{16}O_2$: 204.11448, found 204.11504.

(*E*)-1-(4-Bromophenyl)-4-methylpenta-1,4-dien-3-one[27] (8). Yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 5.86 (s, 1H), 6.03 (s, 1H), 7.28 (d, 1H, J = 15.8 Hz), 7.40−7.46 (d, 2H, J = 8.4 Hz), 7.51−7.61 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 121.7, 124.5, 124.7, 129.6, 132.1, 133.8, 142.1, 145.6, 191.6. MS m/z (rel int): 250 (M^+ 30%), 211 (60), 181 (25), 171 (75), 128 (30), 102 (100), 75 (35). HRMS calcd for $C_{12}H_{11}BrO$: 249.99832, found 249.99933.

(*E*)-1-(4-Chlorophenyl)-4-methylpenta-1,4-dien-3-one[27] (9). Yield: 74%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 5.78−5.79 (m, 1H), 5.96 (s, 1H), 7.19 (d, J = 15.9 Hz, 1H), 7.28−7.31 (m, 2H), 7.43−7.45 (m, 2H), 7.52 (d, J = 15.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6, 121.7, 124.6, 129.1, 133.4, 142.0, 129.4, 136.1, 145.5, 191.5. MS m/z (rel int): 206 (M^+, 20), 171 (50), 165 (100), 137 (50), 102 (45), 76 (15), 50 (10). HRMS calcd for $C_{12}H_{11}ClO$: 206.04984, found. 206.05146

(*E*)-1-(3-Methoxyphenyl)-4-methylpenta-1,4-dien-3-one[27] (10). Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98−2.04 (m, 3H), 3.84 (s, 3H), 5.84−5.85 (m, 1H), 6.03 (s, 1H), 6.94−6.97 (m, 1H), 7.08−7.10 (m, 1H), 7.17−7.24 (m, 2H), 7.26−7.32 (m, 1H), 7.62 (d, J = 15.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 55.3,

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120.9, 113.3, 115.9, 121.6, 124.4, 145.9, 159.6, 129.8, 143.4, 145.5, 192.0. MS m/z (rel int): 202 (M^+, 40), 174 (65), 161 (100), 159 (45), 133 (48), 118 (52), 103 (27), 89 (35), 63 (34). HRMS calcd for $C_{13}H_{14}O_2$: 202.09938, found 202.09914.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra of compounds **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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