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Regiodefined Apparent Hydroallylation toward α,β-Unsaturated Carbonyl Compounds Attained by the Rhodium-Catalyzed One-Pot Procedure

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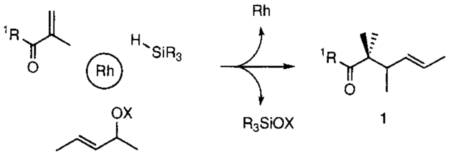
Carbon−carbon bond formation catalyzed by a transition-metal complex is one of the fastest growing fields in synthetic organic chemistry.[1] In particular, it is fascinating that several bonds are formed in an orderly manner in a one-pot reaction of more than three starting substrates under almost neutral conditions.[2] We have found that certain types of rhodium complexes enable multicomponent couplings including a hydrosilane as a starting component.[3] We attempted to design a new type of the rhodium-catalyzed reaction which provides a facile route constructing homoallyl carbonyl compounds **1** (Scheme 1). We report herein the rhodium-catalyzed formal hydroallylation toward α,β-unsaturated carbonyl compounds, which produces **1** in a one-pot reaction of a hydrosilane, an α,β-unsaturated carbonyl compound, and an allylic carbonate.

Scheme 1



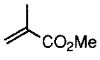
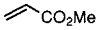
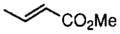
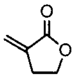
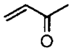
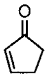
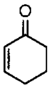
A formal hydroallylation toward an activated alkene was accomplished by the catalysis of a Rh(I) complex. Methyl methacrylate (**2a**) interacted with diethylmethylsilane (**3a**) and 3-methoxycarbonyloxy-1-phenyl-1-butene (**4a**) to form a mixture of **6aa** and **7aa** in a CH_2Cl_2 solution containing these substrates and 1 mol % of $[Rh(COD)(PR_3)_2]OTf$ (**5**, COD = 1,5-cyclooctadiene). As shown in Table 1 (entry 2), $[Rh(COD)(PMePh_2)_2]OTf$ (**5b**) gave an acceptable result though long reaction time was needed for complete consumption of **4a**. It should be noted that these substrates do not interact in the absence of **5** and that either **2a** or **4a** is susceptible to **3a** in the presence of **5**. The corresponding complexes bearing BF_4^- or PF_6^- as an anionic part did not give any product under similar conditions.

Table 1. Hydroallylation of **2a** with **3a** and **4a** Catalyzed by **5**[a]

entry	[Rh] OTf	conditions	products yield[b] (%)	 ratio[c] (**6**:**7**)
1	$[Rh(COD)(DPPB)]OTf$ (**5a**)[d]	80 °C/19 h	55	41:59
2	$[Rh(COD)(PMePh_2)_2]OTf$ (**5b**)	25 °C/42 h	90	38:62
3	$[Rh(COD)(PPh_3)_2]OTf$ (**5c**)	25 °C/4 h	76	34:66
4	$[Rh(COD)\{P(OPh)_3\}_2]OTf$ (**5d**)	25 °C/1 h	38[e]	35:65

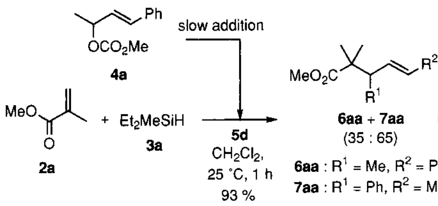
[a] A mixture of **2a** (2 equiv), **3a** (2 equiv), and **4a** was added to a solution of **5** (1 mol % for **4a**) in CH_2Cl_2 at 25 °C and the mixture was stirred for the conditions shown. [b] Isolated yield. [c] Determined by GLC analysis. [d] DPPB = 1,4-bis(diphenylphosphino)butane. [e] In addition to **6aa** and **7aa**, 1-phenyl-1-butene (**8a**) was isolated in 61% yield.

Table 2. Hydroallylation of **2** with **3a** and **4a** Catalyzed by **5d**[a]

entry	substrate **2**		time (h)[b]	products yield[c] (%)	 ratio[d] (**6**:**7**)
				6aa+7aa	
1			1	93	35 : 65
2	**2a**		1	83[e]	32 : 68
3			1	83[f]	35 : 65
				6ba+7ba	
4	**2b**		1	99	33 : 67
				6ca+7ca	
5	**2c**		1	96	51 : 49
				6da+7da	
6	**2d**		2	64	52 : 48
				6ea+7ea	
7	**2e**		1	96[g]	48 : 52
				6fa+7fa	
8	**2f**		1	99	48 : 52
				6ga+7ga	
9	**2g**		12	90	46 : 54

[a] Unless otherwise noted, a solution of **4a** was added at the rate taking about 1 h to a mixture of **2** (2 equiv), **3a** (2 equiv), and **5d** (1 mol %) in CH_2Cl_2 at 25 °C. [b] The time for stirring. [c] Isolated yield. [d] Determined by GLC analysis. [e] Me_2PhSiH was used instead of **3a**. [f] $EtMe_2SiH$ was used instead of **3a**. [g] A mixture of **2e** and **3a** was added to a solution of **4a** and **5d** in CH_2Cl_2.

The rate of this hydroallylation was outstandingly accelerated by tuning the conditions, the use of **5d** as a catalyst, and the slow addition of **4a** into a reaction system (eq 1). The yields of **6aa** and **7aa** increased to 93% (entry 1 in Table 2) when a solution of **4a** in CH_2Cl_2 (4 mL) was slowly added to a CH_2Cl_2 solution of **2a**, **3a**, and **5d** (1 mol % for **4a**) at the rate taking 1 h for completion and then the resulting mixture was stirred for 1 h. In this operation, **8a** was not detected at all. The identical products **6aa** and **7aa** were also selectively obtained in the reactions using Me_2PhSiH (83%, entry 2 in Table 2) or $EtMe_2SiH$ (83%, entry 3 in Table 2) instead of Et_2MeSiH under similar conditions.



(1)

This protocol for the hydroallylation of **2a** is generally applicable to other types of α,β-unsaturated esters and ketones. These results are summarized in Table 2. α-Methylene-γ-

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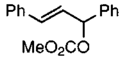
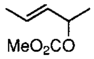
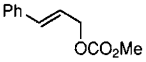
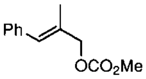
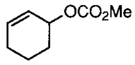
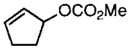
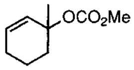
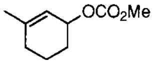
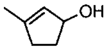
Table 3. Hydroallylation of **2a** with **3a** and **4** Catalyzed by **5d**[a]

entry	4		time[d] (h)	products	yield[b] (%)	ratio[c] (**6** : **7**)
1	**4b**		45	**6ab**	78	–
2	**4c**		6	**6ac**	76	–
3	**4d**		24	**6ad+7ad**	51[c]	58 : 42
4	**4e**		31	**6ae+7ae**	76[c]	56 : 44
5	**4f**		13	**6af**	83	–
6	**4g**		1	**6ag**	62[f]	–
7	**4h**		1	**6ah+7ah**	71	5 : 95
8	**4i**		2	**6ai+7ai**	77	93 : 7
9	**4j**		5	**6aj**	57	100 : 0

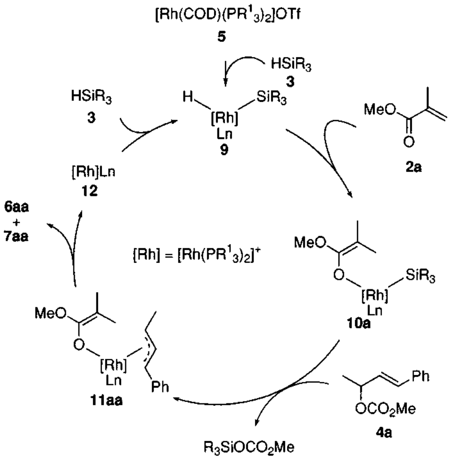
[a] Unless otherwise noted, a solution of **4** was added at the rate taking about 1 h to a mixture of **2a** (2 equiv), **3a** (2 equiv), and **5d** (1 mol %) in CH_2Cl_2 at 25 °C. [b] Isolated yield. [c] Determined by GLC analysis. [d] The time for stirring. [e] A mixture of **2a**, **3a**, and **4** in CH_2Cl_2 was refluxed for the given reaction time in the presence of **5d** (1 mol %). [f] **5c** was used in place of **5d** as a catalyst.

butyrolactone (**2d**) resulted in moderate yields of **6da** and **7da** (entry 6 in Table 2), whereas **2f** and **2g** gave the corresponding products in an excellent yield (entries 8 and 9 in Table 2).

Many types of allylic carbonate behaved as an allylating reagent as well as **4a**, though the reactivity of **4** significantly depends on the structure. The results are summarized in Table 3. Carbonates derived from primary alcohols (**4d** and **4e**) required forcing conditions to form **6** and **7** in acceptable yields (entries 3 and 4 in Table 3). Alicyclic carbonates showed high reactivity comparable to **4a** (entries 5–8 in Table 3). In the reaction of **4g**, less active **5c** was rather suitable than **5d** as a catalyst, since the formation of **6ag** became a minor path in the presence of **5d** despite the fast consumption of **4g** (entry 6 in Table 3). It is worth noting that 3-methyl-2-cyclopentene-1-ol (**4j**) reacted with **2a** and **3a** to give **6aj** in 57% yield as the sole product (entry 9 in Table 3).

The results hitherto described show clearly that the interaction between **2** and **3** on the rhodium metal must have priority over the one between **3** and **4** for accomplishing the selective coupling of these three substrates. It is well-established that the oxidative addition of hydrosilanes to transition metals is an important step in the hydrosilylation of unsaturated bonds.[4] Thus, the following scheme (Scheme 2) can be proposed as a possible rationale for the present coupling in which **2a** and **4a** are presented as a typical example. H–[Rh]–SiR_3 species (**9**, where [Rh] = $[Rh(PR^1_3)_2]^+$) are formed by the oxidative addition of hydrosilane (**3**) to the cationic rhodium complex (**5**) during the first stage. Insertion of an α,β-unsaturated ester (**2a**) to the hydride–rhodium bond of **9** gives the rhodium–enolate species (**10a**).[5,6] Subsequently, the interaction of allylic carbonate (**4a**) with **10a** generates the η^3-allyl rhodium enolate (**11aa**) with the concomitant formation of methyl trialkylsilyl carbonate. Ligand coupling resulting from **11aa** gives a mixture of products (**6aa** and **7aa**) and a low valent rhodium species (**12**) that interacts with **3** to regenerate **9**. Participation of η^3-allyl complex **11** in Scheme 2 is consistent with the fact that a similar result (89% yield, **6aa**:**7aa** = 35:65) was obtained from the reaction of a regioisomer of **4a**, 1-methoxycarbonyloxy-1-phenyl-2-butene (**4a′**).

Scheme 2



In all examples presented here, the α-carbon of **2** is exclusively allylated, whereas the distinction between the two allylic termini is relatively difficult during the reaction of linear carbonates (Table 2 and entries 3 and 4 in Table 3). In contrast, the regiochemistry of the alicyclic ones seems to be remarkably affected by the steric factor. The methoxycarbonyloxy group of **4h** and **4i** was replaced to form a C–C bond at the less substituted terminus of the corresponding allylic group with the high selectivity of 95% and 93%, respectively (entries 7 and 8 in Table 3). Diastereochemistry of the products is not controlled at this stage (entries 4–9 in Table 2). Although access to the similar frameworks is possible through classical methods such as allylation of enolate anions[7] and allylation of enoxysilanes,[8] there is no general and facile methodology to control the regiochemistry and/or the stereochemistry in the substitution at the allylic termini. Therefore, the present three-component coupling retains a sufficient usefulness not only in the novelty of the reaction, but also in synthetic organic chemistry despite these defects.

Acknowledgment. We thank CREST and the Ministry of Education, Science, Sports and Culture for the financial support.

Supporting Information Available: Experimental procedure for the formal hydroallylation of α,β-unsaturated carbonyl compounds and spectral and analytical data for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) A similar sequence is postulated in the reactions constructing aldol-type products from an α,β-enone, a hydrosilane, and an aldehyde.[3m] Rhodium enolate complexes are formed by the interaction of a chlororhodium species with an enolate anion.[5d]

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