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Highly Regio- and Stereoselective Addition of 1,3-Diketones to Internal Alkynes Catalyzed by Cationic Iridium Complex

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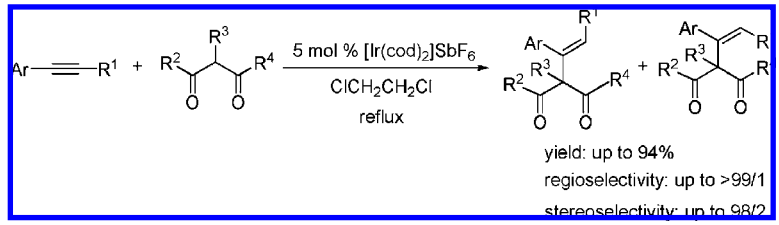
ABSTRACT



The first regio- and stereoselective addition of 1,3-diketones to unfunctionalized internal alkynes under neutral conditions is achieved by using $[Ir(cod)_2]SbF_6$ as a catalyst.

The addition of 1,3-dicarbonyl compounds to carbon−carbon multiple bonds substituted with an electron-withdrawing group has been widely used as the Michael reaction in organic synthesis.[1] Recently, much attention has been paid to the catalytic addition of active methylene compounds to unfunctionalized carbon−carbon double bonds under neutral conditions. Suitable substrates for hydroalkylation have been reported to be alkenes,[2,3] conjugated dienes,[3e,g,4] allenes,[5] and cyclic enol ethers.[3g,4b] Further, intramolecular hydroalkylation to unfunctionalized carbon−carbon double bonds has been reported.[6] Although intramolecular hydroalkylation to carbon−carbon triple bonds, which is known as the Conia-ene reaction, has recently been applied to the synthesis of carbocycles,[7] the addition of an active methylene compound to an unfunctionalized carbon−carbon triple bond under neutral conditions has been unexplored. Applicable alkynes are limited to terminal alkynes.[8,9] Indium triflate[8] and rhenium complexes[9] are used as catalysts for this addition. To expand the reaction scope and enhance the selectivity, a new catalytic reaction is needed. To the best of our knowledge, the addition of 1,3-dicarbonyl compounds to unfunctionalized internal alkynes has not been reported.[10] In the course of our study on iridium-catalyzed carbon−carbon bond formation,[11] we found the first regio- and stereoselec-

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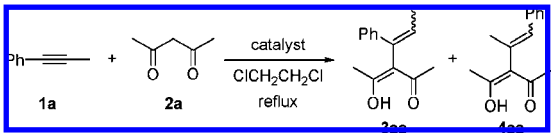
tive addition of 1,3-diketones to unfunctionalized internal alkynes under neutral conditions.

1-Phenyl-1-propyne (**1a**) reacted with acetylacetone (**2a**) in the presence of a catalytic amount of cationic iridium complex under refluxing 1,2-dichloroethane to give **3aa**. The product was obtained as an enol form. Notably, the reaction proceeded under neutral conditions. The catalyst was screened by reacting **1a** with **2a**. The results are summarized in Table 1. A neutral iridium complex $[Ir(cod)Cl]_2$ did not show any catalytic activity for the reaction (entry 1). On the other hand, cationic iridium complexes showed catalytic activity to give **3aa** in good to excellent yields (entries 2−5). The counteranion of these complexes had a profound effect on the reaction. $[Ir(cod)_2]SbF_6$ gave the best result (entry 5). Carbon−carbon bond formation was regiospecific and occurred at the alkyne carbon substituted with a phenyl group. The *E*-selectivity of the newly formed carbon−carbon double bond in **3aa** was 98%. The catalyst loading could be reduced to 5 mol % without reducing the yield or selectivity (entry 6). While the regioselectivities with $[Ir(cod)_2]BF_4$, $[Ir(cod)_2]PF_6$, and $[Ir(cod)_2]OTf$ were the same as that with $[Ir(cod)_2]SbF_6$, the yields and stereoselectivities decreased (entries 2, 3, and 4). $AgSbF_6$ and $NaSbF_6$ did not show any catalytic activity (entries 7 and 8). These results clearly showed that the cationic iridium species was the catalytically active species for this reaction. The use of PPh_3 or $P(OPh)_3$ as an additional ligand inhibited the reaction.

Table 1. The Reaction of 1-Phenyl-1-propyne (**1a**) with Acetylacetone (**2a**)[a]

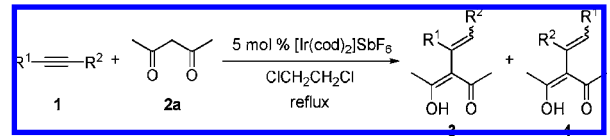


entry	catalyst (loading (mol %))	time (h)	yield (%)[b]	**3aa**/**4aa**[c]	*E*/*Z* of **3aa**[d]
1	$[Ir(cod)Cl]_2$ (4)	24	0		
2	$[Ir(cod)_2]BF_4$ (8)	24	62	>99/1	53/47
3	$[Ir(cod)_2]PF_6$ (8)	24	66	>99/1	56/44
4	$[Ir(cod)_2]OTf$ (8)	1	82	>99/1	58/42
5	$[Ir(cod)_2]SbF_6$ (8)	0.2	92	>99/1	98/2
6	$[Ir(cod)_2]SbF_6$ (5)	1	91	>99/1	96/4
7	$AgSbF_6$ (8)	24	0		
8	$NaSbF_6$ (8)	24	0		

[a] Reaction conditions: **1a** (1.0 mmol) and **2a** (3.0 mmol) in the presence of a catalyst in 1,2-dichloroethane (5 mL). [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] The stereochemistry of **3aa** was determined by NOESY analysis, and the ratio was determined by ^{1}H NMR.

The addition of acetylacetone (**2a**) to various internal alkynes (**1b**−***l***) in the presence of 5 mol % of $[Ir(cod)_2]SbF_6$ under refluxing 1,2-dichloroethane was examined (Table 2).

Table 2. The Reaction of Alkynes (**1a**−***l***) with Acetylacetone (**2a**)[a]



entry	R^1	R^2	**1**	products	time (h)	yield (%)[b]	**3**/**4**[c]	*E*/*Z* of **3**[d]
1	Ph	Me	**1a**	**3aa**, **4aa**	1	91	>99/1	96/4
2	Ph	Et	**1b**	**3ba**, **4ba**	1	76	95/5	91/9
3	Ph	Et	**1b**	**3ba**, **4ba**	2	84	95/5	89/11
4	Ph	*n*Pr	**1c**	**3ca**, **4ca**	1	73	96/4	94/6
5	Ph	*n*Pr	**1c**	**3ca**, **4ca**	12	80	95/5	69/31
6	Ph	*n*Bu	**1d**	**3da**, **4da**	1	64	95/5	92/8
7	Ph	*n*Bu	**1d**	**3da**, **4da**	24	74	95/5	48/52
8	4-chlorophenyl	Me	**1e**	**3ea**, **4ea**	1	88	97/3	98/2
9	4-methylphenyl	Me	**1f**	**3fa**, **4fa**	0.5	90	>99/1	91/9
10	4-methoxyphenyl	Me	**1g**	**3ga**, **4ga**	0.3	92	>99/1	93/7
11	1-naphthyl	Me	**1h**	**3ha**, **4ha**	1	88	99/1	94/6
12	2-naphthyl	Me	**1i**	**3ia**, **4ia**	1	89	>99/1	94/6
13	Ph	Ph	**1j**	**3ja**, **4ja**	1	83		85/15
14[e]	1-cyclohexenyl	Me	**1k**	**3ka**, **4ka**	1	77	>99/1	96/4
15	2-thienyl	*n*Bu	**1*l***	**3*l*a**, **4*l*a**	0.2	82	>99/1	9/91

[a] Reaction conditions: **1** (1.0 mmol) and **2a** (3.0 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.05 mmol) in 1,2-dichloroethane (5 mL). [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] The stereochemistry of **3** was determined by NOESY analysis, and the ratio was determined by ^{1}H NMR. [e] 10 mol % of catalyst was used.

We subjected 1-phenyl-1-alkynes to the reaction to compare the effect of the length of the alkyl substituent. Both the yield and stereoselectivity decreased as the alkyl substituent was extended from methyl to *n*-butyl (entries 1, 2, 4, and

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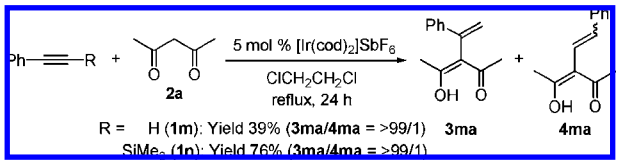
6). The yield decreased from 91% to 64% and the *E*-selectivity decreased from 96% to 92%. Despite this decrease in yield and *E*-selectivity, the regioselectivity was almost the same regardless of the length of the alkyl substituent. A longer reaction time improved the yield, but decreased the *E*-selectivity (entries 3, 5, and 7). We next examined the effect of a substituent on the aromatic ring on the reaction (entries 8−10). The yields were almost the same regardless of the substituent. The reactions of **1f** and **1g** were slightly more regioselective than that of **1e**, while the reaction of **1e** was more stereoselective than those of **1f** and **1g**. 1-(1-Naphthyl)-1-propyne (**1h**), 1-(2-naphthyl)-1-propyne (**1i**), and diphenylacetylene (**1j**) reacted smoothly with **2a** to give the product in yields of 83−89% (entries 11−13). The reaction of conjugated enyne **1k** with **2a** gave the product in 77% yield (entry 14). This result showed that the addition was chemoselective. 1,3-Diketone **2a** added to a carbon−carbon triple bond exclusively. A carbon−carbon double bond was inert for the addition. A heteroaromatic ring was tolerated for the addition. 1-(2-Thienyl)-1-hexyne (**1*l***) reacted with **2a** to give **3*l*a** in 82% yield (entry 15). The stereochemistry of **3*l*a** was unambiguously determined by 2D-NOESY. Although the configuration was assigned to be *Z* by CIP priority rules, the *syn*-addition of **2a** to a carbon−carbon triple bond was the same as those of other alkynes (**1a**−**k**).

We next examined the addition of **2a** to terminal alkynes. Phenylacetylene (**1m**) reacted with acetylacetone (**2a**) under the same reaction conditions as internal alkynes to give **3ma** in 39% yield (Scheme 1). A terminal alkyne did not give a satisfactory yield. We could overcome this drawback by using a trimethylsilyl alkyne as an alternative to a terminal alkyne. The reaction of 1-phenyl-2-trimethylsilylacetylene (**1n**) with **2a** gave **3ma** in 76% yield with perfect regioselectivity (Scheme 1) (vide infra). Carbon−carbon bond formation took place at the alkyne carbon substituted with a phenyl group.

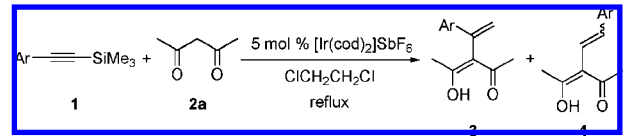
Scheme 1



We examined the chemoselectivity of the reaction (Table 3). Acetyl, ester, and nitro groups were tolerated under the reaction conditions (entries 2, 3, and 4). The products were obtained in yields of 69−81%. Notably, formyl and alkenyl groups were tolerated under the reaction conditions (entries 1 and 5). The reaction of substrates substituted with a formyl group and an alkenyl group gave the respective products in yields of 49% and 60%. 1,3-Diketone **2a** did not add to these functional groups. Good chemoselectivity was observed.

The reaction of 1-phenyl-1-propyne (**1a**) with various 1,3-diketones was studied. The results are summarized in Table 4. The products were obtained in yields of 84−93%. 1,3-Diketone substituted with a bulky group such as isopropyl, *tert*-butyl, or phenyl (**2c**−**e**) smoothly added to **1a** to give

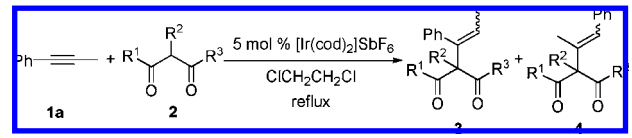
Table 3. The Reaction of Trimethylsilylalkynes (**1o**−**s**) with Acetylacetone (**2a**)[a]

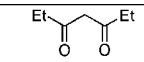
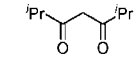
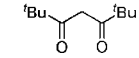
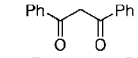
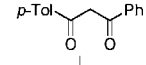
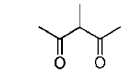
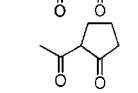
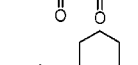


entry	Ar	1	products	time (h)	yield (%)[b]	3/4[c]
1	4-OHC-C_6H_4−	**1o**	**3oa**, **4oa**	5	49	>99/1
2	4-CH_3CO-C_6H_4−	**1p**	**3pa**, **4pa**	24	81	>99/1
3	4-EtO_2C-C_6H_4−	**1q**	**3qa**, **4qa**	24	78	>99/1
4	4-O_2N-C_6H_4−	**1r**	**3ra**, **4ra**	48	69	93/7
5	4-CH_2=CH-C_6H_4−	**1s**	**3sa**, **4sa**	24	60	>99/1

[a] Reaction conditions: **1** (1.0 mmol) and **2a** (3.0 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.05 mmol) in 1,2-dichloroethane (5 mL). [b] Isolated yield. [c] Determined by ^1H NMR.

Table 4. The Reaction of 1-Phenyl-1-propyne (**1a**) with 1,3-Diketones (**2**)[a]



entry	diketones	2	products	time (h)	yield (%)[b]	3/4[c]	*E*/*Z* of **3**[d]
1[e]		**2b**	**3ab**, **4ab**	1	86	>99/1	96/4
2[e]		**2c**	**3ac**, **4ac**	1	84	>99/1	98/2
3		**2d**	**3ad**, **4ad**	1	91	>99/1	1/>99[f]
4		**2e**	**3ae**,[g] **4ae**	0.5	93	>99/1	1/>99
5		**2f**	**3af**, **4af**	1	84	>99/1	1/>99
6		**2g**	**3ag**, **4ag**	1	89	91/9	93/7
7		**2h**	**3ah**, **4ah**	0.5	89	99/1	>99/1
8		**2i**	**3ai**, **4ai**	0.5	91	95/5	95/5

[a] Reaction conditions: **1a** (1.0 mmol) and **2** (3.0 mmol) in the presence of $[Ir(cod)_2]SbF_6$ (0.05 mmol) in 1,2-dichloroethane (5 mL). [b] Isolated yield. [c] Determined by ^1H NMR. [d] The stereochemistry of **3** was determined by NOESY analysis, and the ratio was determined by ^1H NMR. [e] Products were obtained as enol form. [f] The stereochemistry of **3ad** was determined by the $^{13}C-^1H$ coupling constant. [g] The structure of **3ae** was unambiguously determined by X-ray crystallography.[12]

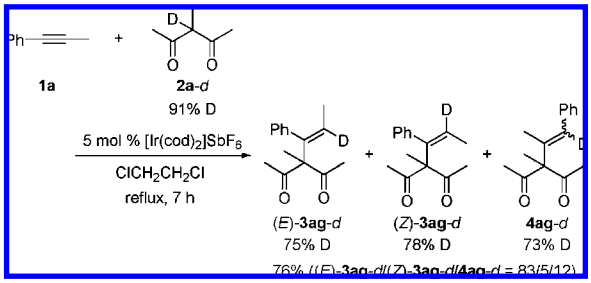
(12) An ORTEP drawing of **3ae** is shown in the Supporting Information as Figure S1.

the respective product (entries 2, 3, and 4). Cyclic 1,3-diketones (**2h**,**i**) as well as acyclic 1,3-diketones (**2a**−**g**) could be used for the addition. The yields with cyclic 1,3-diketones were almost the same as those with acyclic 1,3-diketones (entries 8 and 9). Unsubstituted 1,3-diketones (**2b**−**f**) added to a carbon−carbon triple bond with perfect regioselectivity (entries 1−5). With 2-substituted-1,3-diketones (**2g**−**i**), the addition was less regioselective due to steric hindrance at the 2-position in 1,3-diketone. The regioselectivities were 91−99%. The stereochemistry of **3ad**−**af** was unambiguously determined by 2D-NOESY. Although the configration of **3ad**−**af** was assigned to be *Z* due to CIP-priority rules (entries 3−5), the addition of **2d**−**f** to a carbon−carbon triple bond was *syn*, which was the same as that observed for other 1,3-diketones.

To examine whether (*E*)-**3aa** isomerized to (*Z*)-**3aa** under the reaction conditions, we reacted a 99:1 mixture of (*E*)- and (*Z*)-**3aa** under refluxing 1,2-dichloroethane for 24 h in the presence of 5 mol % of $[Ir(cod)_2]SbF_6$. The *E*/*Z* ratio changed from 99/1 to 39/61. Thus, it is clear that initially formed *E*-product isomerizes to *Z*-product. The addition proceeds via the *syn*-addition of **2a** to a carbon−carbon triple bond.

We next performed a deuterium-labeling experiment. The reaction of 1-phenyl-1-propyne (**1a**) with 3-deuterio-3-methyl-2,4-pentadione (**2g**-*d*, D: 91%) was examined (Scheme 2). The products **3g**-*d* and **4g**-*d* were obtained in 76% yield.

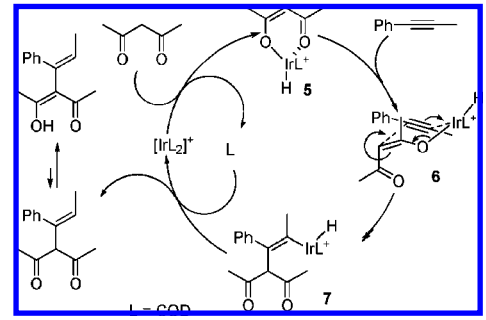
Scheme 2



A deuterium atom was incorporated at the vinyl position (D: 73−78%) exclusively. The decrease in deuterium incorporation in the product can be reasonably explained by the fact that nondeuterium-labeled 1,3-diketones are more reactive than deuterium-labeled 1,3-diketones. The reaction of **1a** with **2g** was completed in 1 h, while the reaction of **1a** with **2g**-*d* was completed in 7 h. The result showed that the reaction of **1a** with **2g** was faster than that of **1a** with **2g**-*d*. Three equivalents of diketone were used for the reaction. Diketone consisted of 2.73 equiv of **2g**-*d* and 0.27 equiv of **2g**, since the deuterium content was 91%. Since 0.27 equiv of **2g** reacted with **1a** faster than 2.73 equiv of **2g**-*d*, the deuterium content in the product decreased from 91% to 73−78%. The *E*-selectivity was 94%, which was the same as that in the reaction with nondeuterium-labeled 1,3-diketone. The position at which a deuterium atom was incorporated clearly suggested that the reaction proceeded via the *syn*-addition of 1,3-diketone to the carbon−carbon triple bond.

A plausible reaction pathway is shown in Scheme 3. A cationic iridium (+1) species reacts with 1,3-diketone to give

Scheme 3



cationic iridium (+3) enolate **5**. The electron deficiency of the cationic iridium species promotes alkyne coordination to give electron-deficient alkyne species **6**,[13] which is highly reactive toward a nucleophile such as a Michael acceptor. Nucleophilic attack of iridium enolate to alkyne gives species **7**. A six-membered transition state facilitates this nucleophilic attack. Reductive elimination from species **7** gives the product. An alkyne carbon substituted with a phenyl group is more electrophilic due to the inductive effect of the phenyl group,[14] and this leads to high regioselectivity for the nucleophilic attack to give **3**.

The reaction of silylalkyne (**1n**) gives a desilylation product (Scheme 1). After the addition of **2a** to **1n**, protodesilylation of a vinylsilane product by HIr^+ species formed from excess **2a** occurs.[15]

In summary, we have developed a regio- and stereoselective addition of 1,3-diketones to unfunctionalized internal alkynes under neutral conditions. Further studies on expanding the scope of this addition are currently in progress.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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