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Rhodium-Catalyzed Addition of α-Keto Acid Chlorides with Terminal Alkynes

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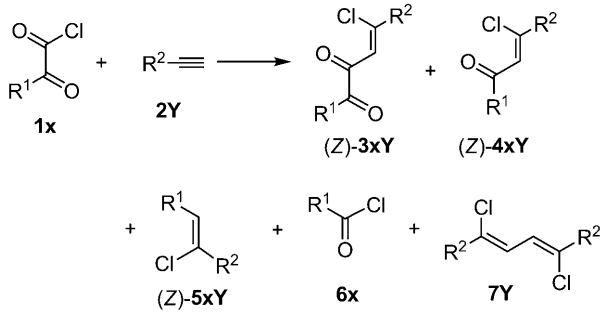
Abstract: The addition reaction of α-keto acid chlorides with terminal alkynes proceeds in the presence of (acetylacetonato)dicarbonylrhodium used as catalyst to afford synthetically versatile (*Z*)-γ-chloro-α-oxo-β,γ-unsaturated ketones regio- and stereoselectively.

Keywords: acylation; alkynes; homogeneous catalysis; ketones; rhodium

Associated with the long known decarbonylation of acid chlorides,[1] addition reactions of aroyl chlorides to alkynes in the presence of rhodium complexes give products coming from formal addition of aryl chlorides.[2] We have reported, however, that acid chlorides, substituted by electron-withdrawing groups, add to alkynes without decarbonylation.[3] In our continued study on the reactivity of acid chlorides with rhodium complexes, we have encountered mono- and dinuclear α-keto acyl rhodium complexes being formed in the reaction of $Rh(acac)(CO)_2$ with α-keto acid chlorides.[4] Although there are several papers reporting on the generation of α-keto acyl complexes, special conditions or procedures to circumvent the difficulty of generation are required in most cases.[5] Accordingly, since the publication of Sen and co-workers,[5e] we have tacitly considered that α-keto acyl complexes are usually thermally labile. With this tacit understanding in mind, our new findings prompted us to scrutinize the possible addition of α-keto acid chlorides to alkynes. This communication discloses that such reactions proceed fairly well to furnish γ-chloro-α-oxo-β,γ-unsaturated ketones (Scheme 1),[6] analogues in the family of synthetically versatile β-chlorovinyl ketones.[3,7]

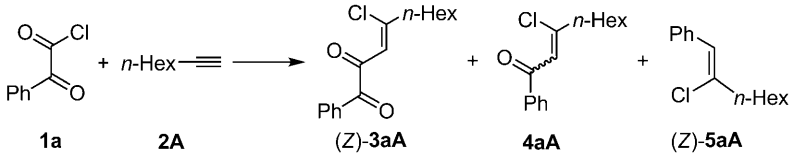
In a representative reaction, a toluene (1.0 mL) solution of phenylglyoxyl chloride (**1a**, 1 mmol), 1-octyne (**2A**, 0.5 mmol) and $Rh(acac)(CO)_2$ (0.025 mmol, 5 mol% relative to **2A**) was heated at 60 °C for 24 h. Analysis of the resulting mixture by GC showed **1a** having been completely consumed to yield (*Z*)-4-chloro-1-phenyl-3-decene-1,2-dione (*Z*)-**3aA** in 70% yield with high regio- and stereoselectivity (Scheme 1; R^1 = Ph, R^2 = *n*-hexyl). An NOE experiment verified the Z stereochemistry (*cis* addition). The regiochemistry was also confirmed by ^1H NMR spectroscopy of the corresponding diol [(*Z*)-**3aA**-red] obtained by reduction with $LiAlH_4$. Besides (*Z*)-**3aA**, by-products such as (*Z*)-**4aA** (trace), (*Z*)-**5aA** (2%), and benzoyl chloride **6a** (30% based on the **1a**), benzophenone (11% based on **1a**), benzil (9% based on **1a**), and (*Z*,*Z*)-7,10-dichlorohexadeca-7,9-diene [(*Z*,*Z*)-**7A**; 9% based on **2A**][8] were also found in the reaction mixture.

Before the $Rh(acac)(CO)_2$ catalyst was determined to be the catalyst of choice, we ran a series of trial experiments under the same conditions as those in the representative reaction (Table 1). Among β-diketonato ligands ($[R^3COCHCOR^4]^-$) screened (entries 1–5),



Scheme 1. Reaction of an α-keto acyl chloride with a terminal alkyne.

Table 1. Trial reactions of **1a** with **2A** under different conditions.[a]



1a **2A** (*Z*)-**3aA** **4aA** (*Z*)-**5aA**

Entry	Catalyst	Time [h]	Conversion [%][b]		Yield [%][b,c]		
			1a	**2A**	(*Z*)-**3aA**	**4aA**	(*Z*)-**5aA**
1[d]	$Rh(acac)(CO)_2$	24	100	94	70	trace	2
2[d]	$Rh(t\text{-BuCOCHCO-}t\text{-Bu})(CO)_2$	24	100	100	73	4	5
3[d]	$Rh(PhCOCHCOPh)(CO)_2$	24	100	100	28	3	11
4[d]	$Rh(CF_3COCHCOCF_3)(CO)_2$	24	100	>99	complex mixture		
5[d]	$Rh(PhCOCHCOMe)(CO)_2$	24	>99	100	45	trace	9
6[d]	$[RhCl(C_2H_4)_2]_2$	24	100	99	31	2	0
7[d]	$[RhCl(cod)]_2$	24	100	100	29	1	1
8[d]	$[RhCl(CO)_2]_2$	24	100	99	21	0	trace
9[d,e]	$Rh(acac)(CO)_2$	24	100	93	63	trace	0
10[d,f]	$Rh(acac)(CO)_2$	24	100	73	48	2	0
11	$Rh(acac)(CO)_2$	24	100	96	52	trace	5
12	$Rh(acac)(CO)(PPh_3)$	24	100	67	29	2	4
13	$Rh(acac)(CO)[P(p\text{-An})_3]$[g]	24	100	60	13	trace	2
14	$Rh(acac)(CO)[P(p\text{-}ClC_6H_4)_3]$[g]	24	100	68	9	trace	6
15	$Rh(acac)(CO)[P(o\text{-Tol})_3]$[g]	24	100	58	10	trace	5
16	$Rh(acac)(CO)[P(m\text{-Tol})_3]$[g]	24	100	51	16	trace	4
17	$Rh(acac)(CO)(PMe_3)$[g]	24	100	49	trace	trace	4
18	$Rh(acac)(CO)(PCy_3)$[g]	24	100	76	2	trace	1
19	$Rh(acac)(CO)(AsPh_3)$	24	100	85	11	trace	6
20	$RhCl(CO)(PPh_3)_2$	24	28	nd[h]	3	7	4
21[i]	$RhCl(CO)(PPh_3)_2$	24	100	85	3	14	38
22[j]	$Rh(acac)(CO)_2$	24	100	100	12	0	15
23[k]	$Rh(acac)(CO)_2$	24	81	67	34	1	1
24[k]	$Rh(acac)(CO)_2$	48	100	100	48	1	trace

[a] *Reaction conditions:* **1a** (1.0 mmol), **2A** (1.0 mmol), catalyst (5.0 mol% in terms of rhodium atom relative to **2A**), toluene (2.0 mL), 60 °C, 24 h.
[b] Determined by GC by using *n*-tetradecane as an internal standard.
[c] Based on **2A** charged.
[d] The quantity of **2A** charged = 0.5 mmol and the quantity of toluene = 1.0 mL.
[e] Run under atmospheric pressure of CO (balloon).
[f] Run under 10 atm of CO.
[g] *In situ* generated by treating $Rh(acac)(CO)_2$ with the respective ligands (1.0 equiv.).
[h] Not determined.
[i] Run at 100 °C.
[j] Run at 70 °C.
[k] Run at 50 °C.

only [*t*-BuCOCHCO-*t*-Bu]$^-$ as ligand displayed nearly the same performance as the [MeCOCHCOMe]$^-$ (acac) ligand to give (*Z*)-**3aA** in 73% yield (*vs.* 70% for acac ligand) and other β-diketonato ligands such as [PhCOCHCOPh]$^-$, [$CF_3COCHCOCF_3$]$^-$ and [PhCOCHCOMe]$^-$ were much inferior. Other rhodium complexes were also active, albeit with a lower efficiency; the yields of (*Z*)-**3aA** were 31% {for [$RhCl(C_2H_4)_2]_2$}, 29% {for $[RhCl(cod)]_2$}, and 21% {for $[RhCl(CO)_2]_2$} (entries 6–8). Attempted reactions run in the presence of atmospheric or pressurized carbon monoxide under otherwise identical conditions, hoping to minimize the formation of miscellaneous by-products stemming from decarbonylation, resulted in a decrease of catalytic activity as compared with entry 1; the yields of (*Z*)-**3aA** were 63% (CO balloon, entry 9) and 48% (10 atm CO, entry 10). The decrease is due most likely to coordination of extra CO ligand to $Rh(acac)(CO)_2$[9] or a detrimental effect against CO dissociation from $Rh(acac)(CO)_2$. Either of these is envisioned to suppress the coordination of alkyne prior to insertion into the Rh–Cl bond (*vide infra*).

Another set of trial experiments was run using **1a** and **2A** (1.0 mmol each) under otherwise identical

conditions (entries 11–19). Among the Rh(acac)(CO)L-type catalysts, $Rh(acac)(CO)_2$ gave the best performance [52% yield of (*Z*)-**3aA**] and other Rh(acac)(CO)L complexes have proved worse to reveal the following trends among ligands; PPh_3 (29%) > P(*m*-Tol)$_3$ (16%) > P(*p*-An)$_3$ (13%) > $AsPh_3$ (11%) ≈ P(*o*-Tol)$_3$ (10%) ≈ P(*p*-ClC_6H_4)$_3$ (9%) > PCy_3 (2%) ≈ PMe_3 (trace). Use of the Vaska-type rhodium complex $[RhCl(CO)(PPh_3)_2]$, which was much less active, resulted in a very messy mixture comprising (*Z*)-**3aA** (3%) and other compounds including (*Z*)- and (*E*)-**4aA**, (*Z*)-**5aA** and **7A** at both 60 and 100 °C (entries 20 and 21). As for the effect of the reaction temperature in $Rh(acac)(CO)_2$-catalyzed reactions (entries 11, 22–24), 60 °C is the optimum temperature affording (*Z*)-**3aA** in 52% yield; another reaction at 70 °C gave (*Z*)-**3aA** in a much lower yield (12%) together with (*Z*)-**5aA** (15%) and a large quantity (39%) of **6a**, while reactions at 50 °C were slow and gave only 34 and 48% yields of (*Z*)-**3aA** even after 24 and 48 h of the reaction time, together with **6a** (48 h: 33%) and traces of (*Z*)-**4aA** and (*Z*)-**5aA**.

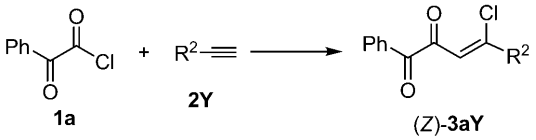
Although we have not examined the effect of solvents in the $Rh(acac)(CO)_2$-catalyzed reaction, toluene appears to be better performing as far as Rh(acac)(CO)(PPh_3)-catalyzed reactions are concerned.[10]

The catalysis by $Rh(acac)(CO)_2$ could be applied readily to other terminal alkynes, yielding the corresponding adducts in acceptable yields with excellent regio- and stereoselectivities (Table 2).

Besides 1-octyne, sterically congested *tert*-butylacetylene also reacts smoothly. Functionalities such as chloro and ester groups bound to aliphatic alkynes are tolerated. Aromatic and heteroaromatic acetylenes also undergo the reaction smoothly. An electronic effect of the *para* substituents is evidently not seen in this catalytic reaction. The reaction of trimethylsilylacetylene is somewhat messy and undergoes rather extensive oligomerization, although the corresponding adduct is obtained in a moderate yield. The reactions of conjugated alkynes (methyl propiolate, 1-ethynylcyclohexene) and internal alkynes (diphenylacetylene, dimethyl acetylenedicarboxylate, 4-octyne), however, are not successful to give benzoyl chloride as major product and oligo- or polymerization of the alkynes also takes place.

1,4-Di(ethynyl)benzene (**2J**) appears to undergo stepwise single and double addition selectively (Scheme 2). Thus, when **2J** was treated with 4 equivalents of **1a**, (*Z*)-**3aJ-1** was formed in 65% NMR yield (62% isolated yield; conversion of **2J** ≈ 100%) nearly as sole adduct. However, nearly the same reaction using 8 equivalents of **1a** furnished (*Z*,*Z*)-**3aJ-2** in

Table 2. Reactions of **1a** with various alkynes **2Y**.[a]

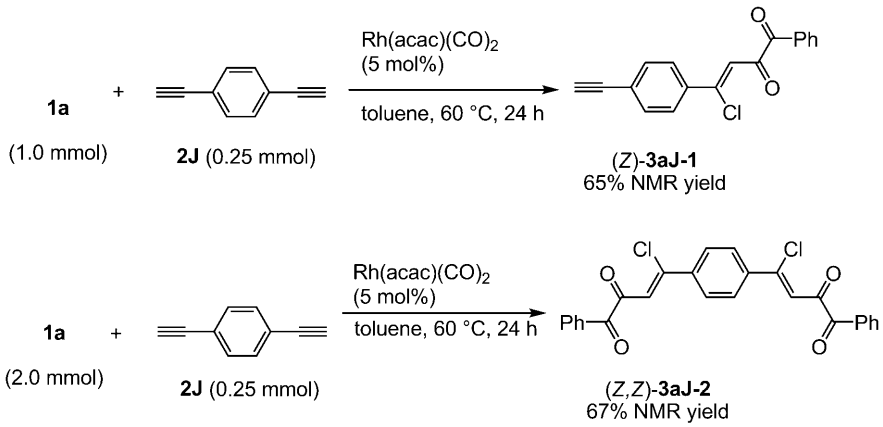


Entry	**2Y**	R^2 =	Yield [%][b]
1	**2A**	*n*-hexyl	70 (66)
2[c]	**2B**	*t*-Bu	68 (67)
3	**2C**	3-chloropropyl	69 (64)
4	**2D**	3-(methoxycarbonyl)propyl	75 (70)
5	**2E**	phenyl	63 (55)
6	**2F**	*p*-methoxyphenyl	65 (61)
7	**2G**	*p*-fluorophenyl	66 (60)
8	**2H**	2-thienyl	81 (75)
9[c]	**2I**	trimethylsilyl	53 (52)

[a] *Reaction conditions:* **1a** (1.0 mmol), **2Y** (0.5 mmol), Rh(acac)(CO)$_2$ (0.025 mmol), toluene (1 mL), 60 °C, 24 h, in a 20-mL Schlenk tube.

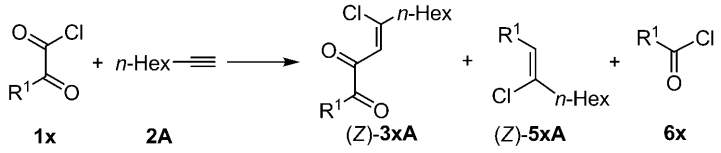
[b] Determined by ^{1}H NMR spectroscopy or GC using 1,1,2,2-tetrachloroethane or *n*-tetradecane, respectively, as internal standard. Based on **2Y**. The figures in parentheses are isolated yields.

[c] Run in a 5-mL Schlenk tube.



Scheme 2. Reactions of 1,4-di(ethynyl)benzene with phenylglyoxyl chloride.

Table 3. Effects of the substituents on α-keto acid chlorides in the reaction with **2A**.[a]



Entry	1x	R^1 =	Yield [%][b]		
			(*Z*)-**3xA**	(*Z*)-**5xA**	**6x**[c] (mmol)[c]
1[d]	**1a**	phenyl	70 (66)	2	0.30
2	**1b**	4-ClC_6H_4	78 (70)	trace	trace
3	**1c**	4-$CF_3C_6H_4$	77 (72)	nd[e]	0.25
5	**1d**	C_6F_5	91 (88)	0	0.01
6[d]	**1e**	*p*-tolyl	trace	43	0.78
7	**1f**	*p*-anisyl	0	18	0.9
8	**1g**	2-thienyl	74 (64)	nd[e]	0.42
9	**1h**	2-furyl	83 (75)	0	nd[e]
10	**1i**	*t*-Bu	21	0	nd[e]

[a] *Reaction conditions:* **1x** (1.0 mmol), **2A** (0.5 mmol), Rh(acac)$(CO)_2$ (0.025 mmol), 60 °C, 24 h in toluene (1 mL).
[b] Determined by ^{1}H NMR spectroscopy or GC using 1,1,2,2-tetrachloroethane or *n*-tetradecane, respectively, as internal standard. The figures in parentheses are isolated yields. Based on **2A**.
[c] Based on **1x** charged and determined by GC using *n*-tetradecane as an internal standard.
[d] A trace of **4xA** was formed.
[e] Not determined.

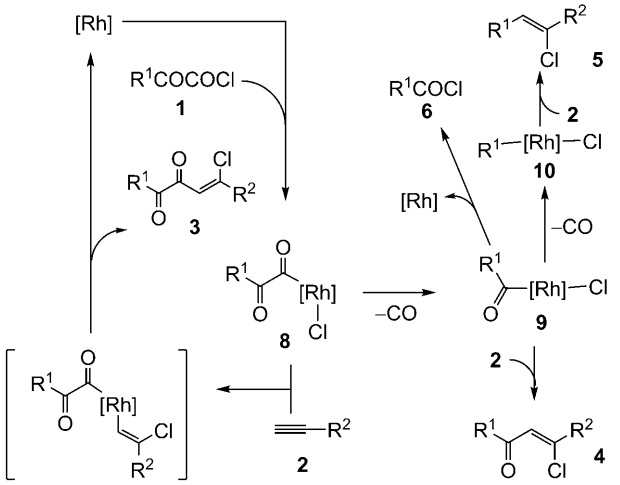
67% NMR yield (58% isolated yield). Although the selective stepwise addition is somewhat puzzling in view of the lack of electronic effects of the *para* substituents of aromatic alkynes on the reactivity, the selectivity suggests that (*Z*)-**3aJ-1** is much less reactive than the starting diyne **2J**.

The reactions of other α-keto acid chlorides are affected significantly by the nature of the substituents (Table 3).

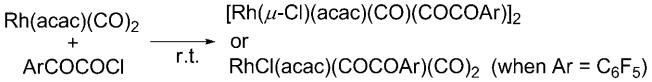
Table 3 shows the yield of **3** decreases in the order of $C_6F_5 > 4\text{-}ClC_6H_4 > 4\text{-}CF_3C_6H_4 > Ph > p\text{-}Tol \geq p\text{-}An$ (≈0), indicating that arylglyoxyl chlorides having electron-withdrawing substituents undergo the reaction smoothly, while those having electron-donating substituents fail to give the desired adducts. Heteroarylglyoxyl chlorides such as **1g** and **1h** also participate in this catalysis smoothly. On the other hand, the reactions of alkyl or alkenyl α-keto acid chlorides are not successful. Although the reaction of 3,3-dimethyl-2-oxobutyryl chloride (**1i**) gave the corresponding product **3** in 21% yield, pyruvoyl chloride gave a very messy mixture. Likewise, the reactions of 3-methyl-3-phenyl-2-oxobutyryl chloride and (*Z*)-4-phenyl-2-oxo-3-butenoyl chloride did not form **3** at all. In the former, the only event observed was the formation of **6** (84%) and in the latter **6** and (*Z*,*Z*)-**7A** were formed in 51 and 32% yields, respectively.

With our previous observations in mind, we propose the mechanism depicted in Scheme 3, which also includes the processes leading to some of the by-products.

As for the initiation process generating intermediate **8**, we have already reported that, with exceptions (*vide infra*), oxidative addition of an arylglyoxyl chloride with Rh(acac)$(CO)_2$ proceeds readily at room temperature to generate arylglyoxylrhodium species (Scheme 4).[4] Insertion of an alkyne into the Rh–Cl



Scheme 3. A plausible mechanism.



Scheme 4. Formation of arylglyoxylrhodium complexes.

bond in **8**[11] and subsequent C–C reductive elimination are also well supported by precedent publications disclosing similar addition reactions of acid chlorides with alkynes[2,3] and chlorinative dimerization of alkynes with trichloroacetyl chloride.[8] To gain further supportive information, we ran a reaction of $[Rh(\mu\text{-}Cl)(acac)(CO)(COCOPh)]_2$ with **2A** {mole ratio of $[Rh(\mu\text{-}Cl)(acac)(CO)(COCOPh)]_2$/**2A** = 0.5} in benzene-d_6 for 24 h at 60 °C. The reaction gave (*Z*)-**3aA** (38%), (*Z*,*Z*)-7,10-dichlorohexadeca-7,9-diene [(*Z*,*Z*)-**7A**; 9% based on **2A**] and benzil (trace).

According to our previous paper, $[Rh(\mu\text{-}Cl)(acac)(CO)(COCOAr)]_2$ (Ar = Ph, *p*-ClC_6H_4) is thermally stable at room temperature, but it does undergo decarbonylation and reductive elimination to give ArCOCl at higher temperatures, e.g., at 60 °C.[4] Complex **8** generated under the present catalytic conditions is also envisioned to experience the same events to give **6** as a by-product. Indeed, all reactions starting with **1a**–**1g** gave aroyl chlorides (**6a**–**6g**), although the extent of their formation depended on the substituent on the aromatic ring as shown in Table 3 (*vide infra*). Since oxidative addition of **6** with $Rh(acac)(CO)_2$ is not a thermodynamically favored process,[4] once compound **6** has been extruded from **9**, regenaration of **9** through the backward process can take place only marginally.

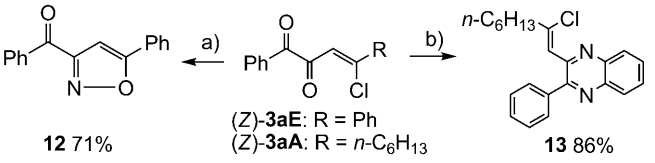
What merits further mechanistic consideration is the origin of the unsuccessful reactions. As is seen in Table 3, arylglyoxyl chlorides having a more electron-donating substituent, **1e** and **1f**, behaved differently from those having an electro-neutral or more electronegative substituent, **1a**–**1d**, in terms of the following three aspects. (i) They did not form **3** in a significant quantity, and (ii) the formation of **6** was more extensive. This reactivity trend agrees with our previous observation that, unlike the reaction of **1a**, for instance, the reaction of **1f** with $Rh(acac)(CO)_2$ at room temperature (in the absence of an alkyne) did not form stable $[Rh(\mu\text{-}Cl)(acac)(CO)(COCO(p\text{-anisyl})]_2$, but proceeded all the way to *p*-anisoyl chloride and $Rh(acac)(CO)_2$, indicative of rapid decarbonylation from *p*-AnCOCORhCl to *p*-AnCORhCl and reductive elimination.[4] (iii) Only **1e** and **1f** formed **5** in appreciable quantities. As is mentioned in the introduction section, we have reported that electron-withdrawing substituents bound to acid chlorides suppress the decarbonylation from RCORhCl to RRhCl.[3,12] Intermediate species **9e** and **9f** (R^1 = *p*-Tol, *p*-An), however, are substituted by electron-donating substituents. Accordingly, the electronic nature is envisioned to, at least partially, give an advantage to decarbonylation forming **10** in competition with the rapid reductive elimination forming **6**. Conversion of **9** to **10** is made easier for **1e** and **1f**, as compared with **1a**–**1d**, and leads to the formation of **5** as Miura and co-workers reported.[2]

In the present catalysis, other by-products such as benzil, benzophenone and 1,4-dichloro-1,3-butadiene derivatives were also formed in small quantities. One can think of a bimolecular reductive elimination from or a disproportionation of intermediates **8**, **9** and/or **10** as candidate pathways to these by-products. Indeed, *p*-chloro analogues of benzil and benzophenone were formed in the thermolysis of *p*-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$, but not in the thermolysis of $[Rh(\mu\text{-}Cl)(acac)(CO)(COCO(p\text{-}ClC_6H_4)]_2$.[4] The provenance of these by-products is uncertain at the present time.

After the addition of α-keto acid chlorides with alkynes had been realized, it appeared intriguing to attempt the carbonylative addition of benzoyl choride **6a** with 1-octyne **2A**, since we have observed that carbonylation of *p*-$ClC_6H_4CORhCl_2(CO)(PMe_3)_2$ generates *p*-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$, albeit in a low yield.[4] Indeed, a preliminary reaction of **6a** with **2A** under CO atmosphere (50 atm) in the presence of $Rh(acac)(CO)(AsPh_3)$ (5 mol%) at 100 °C for 12 h in toluene gave (*Z*)-**3aA** in 21% GC yield, which encouraged us to further studies, although the yield is not satisfactory at this stage.

The products prepared by the new procedure are quite useful to synthesize, for instance, heterocyclic compounds. The utility of the products can be readily exemplified with (*Z*)-**3aA** and (*Z*)-**3aE**. The former cyclizes with hydroxylamine to afford isoxazole **12**[7] and the latter with *o*-phenylenediamine to afford quinoxaline derivative **13** (Scheme 5).

In conclusion, $Rh(acac)(CO)_2$ catalyzes the addition of α-keto acid chlorides to terminal alkynes stereo- and regioselectively to give β-chlorovinyl α-diketones, which are useful synthetic intermediates. Further investigations on catalyzed addition reactions of acid chlorides, under carbonylative conditions in particular, are in progress.



Scheme 5. Examples of the utility of the products.

Experimental Section

Typical Procedure for the Catalytic Addition Reaction and Isolation of Products: Reaction of 1-Octyne with Phenylglyoxyl Chloride

To a solution of $Rh(acac)(CO)_2$ (6.49 mg, 0.025 mmol) in toluene (1 mL) placed in a 20-mL Schlenk tube were added

phenylglyoxyl chloride (**1a**; 169.2 mg, 1.0 mmol) and 1-octyne (**2A**; 74 μL, 0.5 mmol) and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, *n*-tetradecane (14.6 mg; internal standard for GC analysis) was added to the resulting mixture. After GC analysis, which showed the formation of (*Z*)-**3aA** in 70% yield, the mixture was evaporated and 1,1,2,2-tetrachloroethane (9.9 mg; internal standard for NMR analysis) was added. After NMR analysis, the mixture was evaporated once again and the residue was subjected to column chromatography (silica gel, hexane/acetone = 95/5) to furnish (*Z*)-**3aA**; yield: 66%; yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.97$ (d, $J = 1.45$ Hz, 2H, *o*-Ph), 7.62 (t, $J = 1.90$ Hz, 1H, *p*-Ph), 7.48 (d, $J = 1.45$ Hz, 2H, *m*-Ph), 6.70 (s, 2H, C*H*), 2.53 (t, $J = 6.27$ Hz, 2H, C-5), 1.65 (quint, $J = 7.29$ Hz, 2H, C-6), 1.36–1.27 (br-m, 6H, C-7, C-8, C-9), 0.88 (t, $J = 6.78$ Hz, 3H, C-10); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 192.0$ (CO), 190.6 (CO), 154.9 (C-4), 134.4 (*p*-C), 132.3 (*ipso*-C in Ph), 130.1 (*o*-C), 128.7 (*m*-C), 121.0 (C-3), 41.6 (C-5), 31.3 (C-8), 28.2 (C-7), 27.2 (C-6), 22.4 (C-9), 13.9 (C-10); IR (neat): $\nu = 1726$ (ν_{CO}), 1674 (ν_{CO}), 1597 cm^{-1} ($\nu_{C=C}$); GC-MS (70 eV): *m/z* (% relative intensity) = 278 ([M]$^+$, 5), 250 (26), 201 (15), 173 (16), 132 (62), 105 (100), 77 (34); HR-MS (EI): *m/z* = 278.1069, calcd. for $C_{16}H_{19}ClO_2$: 278.1074. An NOE experiment displayed 12.2% enhancement of the vinylic proton signal ($\delta = 6.70$ ppm) upon irradiation at the allylic proton signal (2.53 ppm), indicative of *cis* addition having taken place.

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