Nickel-Catalyzed Formation of Cyclopentenone Derivatives via the Unique Cycloaddition of α,β-Unsaturated Phenyl Esters with Alkynes

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S *Supporting Information*

ABSTRACT: Oxygen-containing organic compounds, such as ethers, carboxylates, and carbamates, have recently received increasing attention because of their newly discovered applications as electrophiles in cross-coupling reactions via transition metal-catalyzed C−O bond activation. However, no cycloaddition reaction involving their C−O bond activation has been demonstrated thus far. The present study developed a Ni(0)-catalyzed unique [3+2] cycloaddition reaction of α,β-unsaturated phenyl esters with alkynes in ^{i}PrOH to yield cyclopentenone derivatives.

Transition metal-catalyzed cycloaddition is one of the most powerful strategies for one-step preparation of a variety of cyclic compounds. Nickel(0) complexes have also been known to catalyze cycloaddition reactions efficiently in various manners, wherein a wide variety of combinations of unsaturated organic compounds are used as a substrate.[1] In the course of our continuous studies on development of nickel-catalyzed C−C bond formation reactions and isolation of nickelacycle key intermediates,[2] we recently demonstrated a nickel-catalyzed [3+3] cyclodimerization reaction of alkylidenecyclopropanes such as ethyl cyclopropylideneacetate (**1a**) via cleavage of a proximal C−C bond to yield 1,2-bis-*exo*-alkylidenecyclohexanes in excellent yields.[3,4] However, a crucial difference was found in the reactivity between the alkyl ester **1a** and the corresponding phenyl ester **1b**, which gave a trace amount of the corresponding [3+3] cycloaddition product **2b**. To elucidate the difference in detail, a stoichiometric reaction of **1b** with Ni(cod)$_2$ in the presence of PCy$_3$ was carried out. As a result, a small amount of a mixture containing the [3+3] cycloaddition product **2b** and the unanticipated spiro[2.5]octane derivative **3** was obtained (eq 1),

(1)
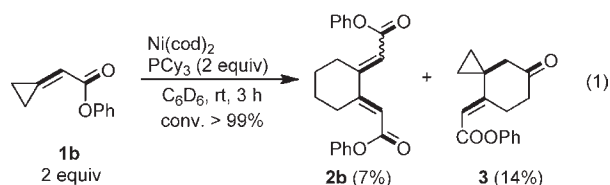
and a "dephenoxylated fragment of **1b**" constituted the six-membered ring in **3** (Chart 1). Although aryl carboxylates have recently received increasing attention because they can participate in catalytic cross-coupling reactions by way of C$_{acyl}$−O activation[5] as well as C$_{aryl}$−O activation,[6,7] no cycloaddition reaction of aryl carboxylates involving their carbon−oxygen bond cleavage has

been reported thus far. Therefore, the present study was focused on whether the dephenoxylated three-carbon unit derived from the C$_{acyl}$−O bond cleavage of α,β-unsaturated phenyl ester could act as a coupling partner with the other unsaturated compounds.

When the stoichiometric reaction of **1b** with 3-hexyne (**4a**) was conducted in C$_6$D$_6$ at room temperature in the presence of Ni(cod)$_2$ and PCy$_3$, the five-membered cycloaddition product **5** was formed in 39% yield (Scheme 1).[8] Furthermore, a cyclopropyl ring is not essential for the reaction; both phenyl cinnamate (**6a**) and phenyl crotonate (**6b**) could be applied to the dephenoxylative coupling reaction to yield the corresponding cyclopentenone derivatives (**7aa** and **7ba**) in 44 and 42% yield, respectively (Scheme 1). Next, based on these stoichiometric findings, the catalytic reaction of **6a** with **4a** by using ^{i}PrOH as a solvent was examined with the anticipation that an alcoholic hydroxyl group would serve as a hydrogen source (Table 1). As a result, elevating the reaction temperature to 130 °C furnished the desired product in 48% yield (run 2), whereas only 10% (the same amount as catalyst) of **7aa** was obtained at room temperature (run 1). A quantitative formation of **7aa** was achieved by the addition of zinc powder (4 equiv, run 3), though a reaction temperature of 130 °C was required (runs 4 and 5). The product **7aa** was not generated at all in the absence of either Ni(cod)$_2$ or PCy$_3$ (runs 6 and 7), but a transesterification reaction occurred in run 7, giving isopropyl cinnamate. In addition, a significant decrease in the yield of **7aa** was observed with the use of 1 equiv of **4a** due to the undesired transesterification reaction (run 8). The effects of both solvent and ligand on this reaction were investigated. Although the use of ^{s}BuOH allowed the reaction to give **7aa** in moderate yield (run 9), neither ^{t}BuOH nor PhOH was effective (runs 10 and 11). The use of aprotic solvents such as toluene and DME gave a small amount of **7aa** (runs 12 and 13). Under the reaction conditions using ^{i}PrOH as a solvent at 130 °C, the use of either PCyp$_3$ (Cyp = c-C$_5$H$_9$) or IPr instead of PCy$_3$ as a ligand afforded **7aa** in 90 and 82% yield, respectively (runs 14 and 15). The use of other phosphine ligands such as PPh$_3$ and P^{n}Bu$_3$, however, retarded the reaction (runs 16 and 17). Neither NiCl$_2$/PCy$_3$ nor Ni(acac)$_2$/PCy$_3$ catalyzed the reaction under the same reaction conditions.

With the optimized reaction conditions represented in run 3 (Table 1), the scope of the Ni(0)-catalyzed dephenoxylative cycloaddition reaction with respect to various alkynes was investigated using **6a** as an α,β-unsaturated phenyl ester. Treatment of **6a** with **4a** in ^{i}PrOH at 130 °C for 3 h gave **7aa** in 91%
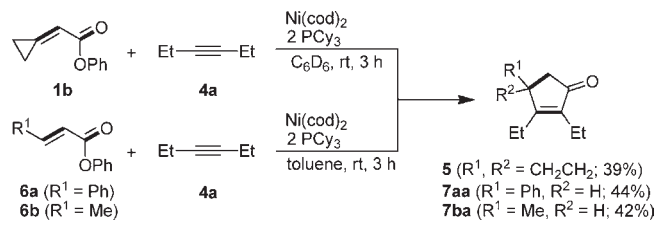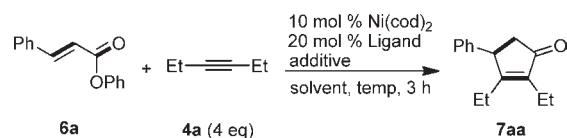
Chart 1. Unanticipated Dephenoxylated Cyclodimerization of 1b To Give a Spiro[2.5]octane Derivative 3
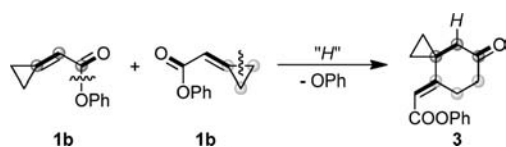
Scheme 1. Stoichiometric Dephenoxylative Cycloaddition of α,β-Unsaturated Phenyl Esters with 3-Hexyne

Table 1. Ni(0)-Catalyzed Dephenoxylative Cycloaddition Reaction of Phenyl Cinnamate 6a with 3-Hexyne 4a[a]


run	additive	ligand	solv	temp (°C)	conv (%)[b]	yield (%)[b]
1	none	PCy₃	^{i}PrOH	rt	12	10
2	none	PCy₃	^{i}PrOH	130	>99	48
3	zinc (4 equiv)	PCy₃	^{i}PrOH	130	>99	>99 (91)
4	zinc (4 equiv)	PCy₃	^{i}PrOH	90	51	39
5[c]	zinc (4 equiv)	PCy₃	^{i}PrOH	rt	30	10
6[d]	zinc (4 equiv)	PCy₃	^{i}PrOH	130	30	–
7[e]	zinc (4 equiv)	–	^{i}PrOH	130	>99	–
8[f]	zinc (4 equiv)	PCy₃	^{i}PrOH	130	>99	65
9[g]	zinc (4 equiv)	PCy₃	^{s}BuOH	130	63	45
10	zinc (4 equiv)	PCy₃	^{t}BuOH	130	16	5
11	zinc (4 equiv)	PCy₃	PhOH	130	<1	–
12	zinc (4 equiv)	PCy₃	toluene	130	18	14
13	zinc (4 equiv)	PCy₃	DME	130	27	8
14	zinc (4 equiv)	PCyp₃	^{i}PrOH	130	>99	90
15	zinc (4 equiv)	IPr	^{i}PrOH	130	>99	82
16	zinc (4 equiv)	PPh₃	^{i}PrOH	130	31	9
17	zinc (4 equiv)	P^{n}Bu₃	^{i}PrOH	130	73	19

[a] General conditions: phenyl cinnamate (0.10 mmol), solvent (5 mL). [b] The conversion of phenyl cinnamate and the yield of the product were determined by GC analysis using C₁₄H₃₀ as an internal standard. The value in parentheses was of isolated yield. [c] Run for 24 h. [d] Run in the absence of Ni(cod)₂. [e] Run in the absence of additional ligands. [f] Run using 1 equiv of 3-hexyne. [g] Formation of 2-butanone was detected by GC analysis.

isolated yield (Table 1, run 3). The reactions with 2-butyne (**4b**) and 4-octyne (**4c**) gave the corresponding cyclopentenone derivatives **7ab** and **7ac** in 84 and 66% yield, respectively (Table 2, runs 1 and 2), while the reaction with 5-decyne (**4d**) gave only an 8% yield of **7ad** (run 3). Use of diphenylacetylene

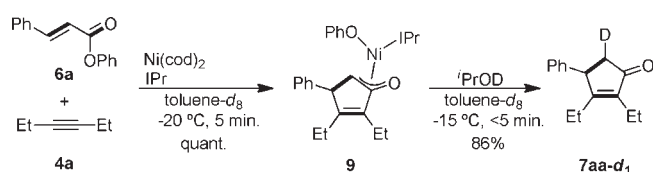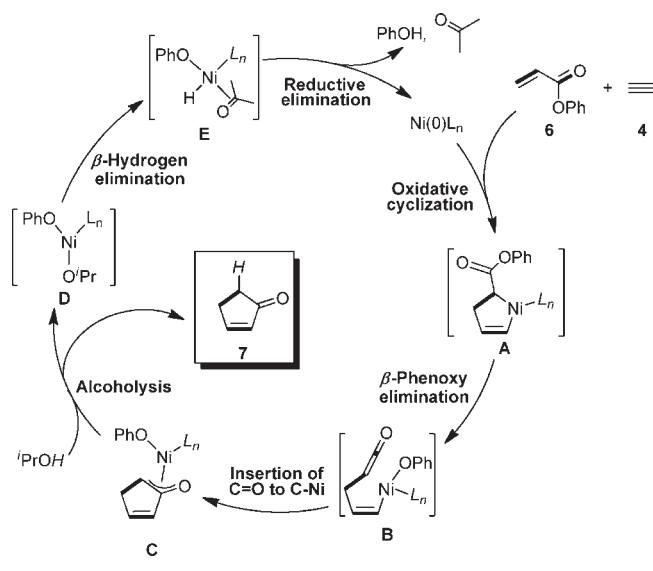**Table 2. Ni(0)-Catalyzed Dephenoxylative Cycloaddition Reaction of α,β-Unsaturated Phenyl Ester 6 with Alkyne 4[a]**
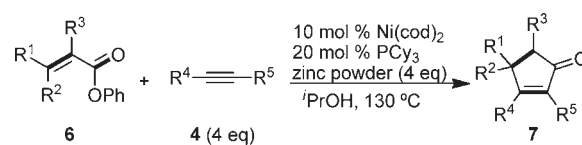
run	phenyl ester (6)			alkyne (4)		time	product (7)
	R¹	R²	R³	R⁴	R⁵		yield (%)[b]
1	6a	Ph	H	H	4b	Me	Me	3 h	7ab 84
2	6a				4c	^{n}Pr	^{n}Pr	6 h	7ac 66
3	6a				4d	^{n}Bu	^{n}Bu	3 h	7ad 8[c]
4	6a				4e	Ph	Ph	3 h	7ae 64
5	6a				4f	^{i}Pr	Me	6 h	7af 70 (66:34)
6	6a				4g	^{n}Pr	Me	6 h	7ag 52 (72:28)
7	6a				4h	Me	Ph	5 h	7ah 64[d]
8	6a				4i	Et—		8 h	7ai 19[d]
9	6a				4j	^{n}Bu	H	6 h	7aj 30[d]
10	6a				4k	Ph	H	3 h	7ak –
11	6a				4l	TMS	H	3 h	7al –
12	6a				4m	TMS	Me	3 h	7am –
13	6a				4n	TMS	Ph	3 h	7an –
14	6b	Me	H	H	4a	Et	Et	3 h	7ba 86
15	6c	^{n}Pr	H	H	4a			6 h	7ca 79
16	6d	^{i}Pr	H	H	4a			8 h	7da 84
17	6e	^{t}Bu	H	H	4a			8 h	7ea 57
18	6f	Cy	H	H	4a			8 h	7fa 49
19	6g	H	H	H	4a			3 h	7ga 14[c]
20	6h	H	H	Me	4a			3 h	7ha 62
21	6i	Me	Me	H	4a			3 h	7ia –
22	6j	Me	H	Me	4a			3 h	7ja –

[a] General conditions: phenyl esters (1.0 mmol), ^{i}PrOH (15 mL). [b] Isolated yields. The values in parentheses were of the ratio of regioisomers (determined by ¹H NMR). [c] GC yields by using C₁₄H₃₀ as an internal standard. [d] GC analysis of the crude product revealed the formation of a mixture of regioisomers (major/minor = 97/3 in the case of **4h**, 99/1 in the case of **4i**, and 76/24 in the case of **4j**), and purification by column chromatography led to the isolation of the corresponding major isomers with the represented formula.

(**4e**) allowed the reaction with **1a** to afford **7ae** (run 4). The reactions with unsymmetrical internal alkynes, such as 4-methyl-2-pentyne (**4f**) and 2-hexyne (**4g**), also proceeded to give **7af** (64%) and **7ag** (52%), respectively, as a mixture of regioisomers (runs 5 and 6). In contrast, the reactions using 1-phenyl-1-propyne (**4h**) and 2-methyl-1-hexen-3-yne (**4i**) gave the corresponding mixtures with excellent regioselectivity, and each major isomer (**7ah** and **7ai**) was isolated in 64 and 19% yield, respectively (runs 7 and 8). The regioselectivity of the reaction with **4h** and **4i** is much better than that with **4f** and **4g**, probably due to the contribution of either an η^{3}-benzyl or an η^{3}-allyl structure in a possible intermediate.[2l,9c] On the other hand, of the terminal alkynes used, only 1-hexyne (**4j**) reacted with **1a** to furnish the corresponding mixture of regioisomers (runs 9–11). In addition, the reactions with silylacetylenes (**4m,n**) were all futile (runs 11–13).

Scheme 2. Observation of the η^3-Oxaallyl Phenoxynickel Intermediate

Scheme 3. A Plausible Reaction Mechanism

the reaction using IPr, which is also a good ligand for the catalytic reaction (Table 1, run 15), at −20 °C was found to generate a phenoxynickel(II) intermediate (**9**) in which a cyclopenta-1,4-dienolate fragment was coordinated to the nickel in η^3-oxaallyl fashion (Scheme 2).[11] Complex **9** was found to be stable in toluene below −20 °C,[12] and its structure was confirmed on the basis of characteristic ^{13}C NMR resonances attributable to the *ipso*-PhONi (δ_C 170.7)[13] and the η^3-oxaallyl moieties (δ_C 162.9 and 81.8).[21] Treatment of **9** with ^{i}PrOD (>98% D) at −15 °C resulted in a clean formation of the corresponding cyclopentenone with a deuterium (98% D) at the 5-position (**7aa-d_1**).

Based on these observations, a plausible mechanism for the Ni-catalyzed dephenoxylative cycloaddition reaction is depicted in Scheme 3.[14,15] The oxidative cyclization of an α,β-unsaturated phenyl ester **6** and an alkyne **4** with nickel(0) takes place to give a nickelacyclopentene intermediate (**A**). The intermediate **A** would undergo β-phenoxy elimination[16] to give a transient ketene intermediate (**B**) which might be converted into an η^3-oxaallyl phenoxynickel species (**C**) corresponding to **9** via insertion of the ketene moiety into the C−Ni bond. Alcoholysis of **C** provides **7** along with the formation of a nickel(II) alkoxide (**D**).

The β-hydrogen elimination followed by reductive elimination would regenerate a nickel(0) species with concomitant generation of acetone and phenol. Although acetone could not be detected in any crude products of the optimized catalytic reactions, this step is supported by the generation of 2-butanone (Table 1, run 9). Since a stoichiometric amount of **7aa** was obtained below room temperature (Scheme 2), a high reaction temperature (130 °C) in this catalytic reaction would be required to regenerate a nickel(0) species. The role of zinc powder as an additive might be explained as either accelerating the reductive elimination step of phenol or directly reducing the nickel(II) intermediate **D** to a nickel(0) species.

In summary, we demonstrated the unique reactivity of α,β-unsaturated phenyl esters to serve as a three-carbon atom unit in nickel-catalyzed cycloaddition reactions, as a result of the selective C_{acyl}−O bond cleavage on nickel. A novel [3+2] cycloaddition reaction with alkyne in the presence of ^{i}PrOH and zinc powder was successfully applied to yield cyclopentenone derivatives in excellent yield.

The scope of the reaction with respect to α,β-unsaturated phenyl esters was further examined. The reaction of **4a** with **6b** gave the corresponding product **7ba** in 86% isolated yield (Table 2, run 14). A variety of (*E*)-disubstituted α,β-unsaturated phenyl esters (**6c**−**f**) also reacted with **4a** to afford the corresponding cyclopentenone derivatives (**7ca**−**fa**) in moderate to high yields (runs 15−18). However, the reaction of phenyl acrylate (**6g**) with **4a** gave **7ga** in low yield, probably due to the rapid oligomerization of **6g** (run 19). This catalytic system was also successfully applied to phenyl methacrylate (**6h**), yielding **7ha** in moderate yield (run 20). However, trisubstituted α,β-unsaturated phenyl esters, such as phenyl senecioate (**6i**) and phenyl tiglate (**6j**), did not give the corresponding cyclopentenones (runs 21 and 22).

It should be emphasized that the reactivity of phenyl ester **6b** was found to be quite different from those of the corresponding ethyl ester and enal; the reaction of ethyl (*E*)-2-butenoate with **4a** in the presence of a catalytic amount of Ni(cod)$_2$ and PCy$_3$ in toluene gave an acyclic hexatriene, whereas the reaction of (*E*)-2-butenal with **4a** did not proceed under the same reaction conditions.[21] In addition, when vinyl cinnamate (**8**) was treated with **4a** under the optimized catalytic reaction conditions, the corresponding devinyloxylative cycloaddition took place to give **7aa** in 18% yield.[10] The conversion of **8** was 71%, and the major product was isopropyl cinnamate.

To elucidate the mechanism for this catalytic reaction, the stoichiometric reaction of **4a** and **6a** with Ni(cod)$_2$ was monitored at low temperature by NMR spectroscopy. Although the use of PCy$_3$ as a ligand did not show any significant intermediates,

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental procedures; analytical and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The other alternative mechanism, which involves alcoholysis of **A** followed by ester carbonyl insertion into the Ni–C bond and β-phenoxy elimination, might be unlikely because it does not involve the formation of intermediate **C**. See Supporting Information as well as related [3+2] cycloaddition references:(a) Herath, A.; Montgomery, J. *J. Am. Chem. Soc.* **2006**, *128*, 14030–14031. (b) Chang, H.-T.; Jayanth, T. T.; Wang, C.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **2007**, *129*, 12032–12041.

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