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Ni-Catalyzed Formal Carbonyl-Ene Reaction of Terminal Alkenes via Carbon Dioxide Insertion

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Abstract Nickel catalyzes the multicomponent coupling reaction of terminal alkenes, carbon dioxide, and organoaluminum reagents, leading to the synthesis of homoallylic alcohols in moderate-to-good yields with excellent regio- and stereoselectivities.

Key words nickel catalyst, carbon dioxide, carbonyl-ene, ketone, organoaluminum

In modern organic chemistry, carbonyl-ene reactions are important and efficient synthetic tools for C–C bond formation using alkenes and carbonyl compounds.¹ In general, combinations of electron-rich alkenes, such as di- or multialkylated substituted alkenes, and more electron-deficient carbonyl compounds, such as glyoxylates and trifluoropyruvates, are effective for C–C bond construction.² Carbonyl-ene reactions involving ketones as the enophiles are less useful than those involving aldehydes owing to lower electrophilicity.³ Therefore, it is necessary to activate the ketones by introducing electron-withdrawing substituents or with highly reactive Lewis acids for more sophisticated C–C bond constructions.

Carbon dioxide is a useful carbon resource owing to its nontoxicity, abundance, and availability.⁴ Therefore, transformation of carbon dioxide to various functional groups can be a convenient and practical method to utilize this useful carbon feedstock. However, most examples of using carbon dioxide have led to the formation of carboxylic acids,⁵ although the transformation of carbon dioxide to other functional groups also deserves attention not only to enhance the synthetic availability of carbon dioxide but also for the development of carbon dioxide fixation processes.⁶



cat. Ni(cod)₂/PCv



Scheme 1 Ni-catalyzed carbonyl-ene-type reaction of monosubstituted alkenes with aldehydes in the presence of triethylsilyl triflate

Ni-catalyzed C-C bond formation is one of the most useful synthetic tools for accessing complicated pharmaceutical compounds and fine chemicals.⁷ We have developed Ni-catalyzed multicomponent coupling reactions of unsaturated hydrocarbons, such as conjugated dienes and enynes, and carbonyl compounds with organometallic reagents as alkyl, aryl, and hydride sources that give highly functionalized organic compounds in a single manipulation.⁸ Recently, Jamison reported the carbonyl-ene reaction of monosubstituted alkenes with aliphatic and aromatic aldehydes that involved a Ni catalyst and was promoted by triethylsilyl triflate (Scheme 1).9 In this case, the regioselectivities depended on the phosphine ligand; PCv₂Ph led to allylic alcohols, whereas PPh₃ led to homoallylic alcohols. Herein, we introduce the Ni-catalyzed multicomponent coupling reaction of terminal alkenes, carbon dioxide, and trimethylaluminum, leading to the synthesis of homoallylic alcohols (Scheme 2). This transformation can be regarded as a formal carbonyl-ene reaction of simple alkenes with ketones to form homoallylic alcohols with high regio- and stereoselectivities in a single operation.





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The reaction was conducted using allylbenzene, Me₃Al, and a catalytic amount of Ni(cod)₂ and various ligands in 1,4-dioxane under a carbon dioxide atmosphere. The results are summarized in Table 1. Monodentate arylphosphine ligands such as PPh₃ were ineffective for the coupling reaction (entry 1, Table 1). With trialkylphosphines such as $P(n-Bu)_3$ and $PCyp_3$, the three-component coupling reaction of allylbenzene, Me₃Al, and carbon dioxide proceeded to give the expected homoallylic alcohol 3aa in moderate yields with small amounts of allylic alcohol 4aa as a minor product (entries 2 and 3, Table 1). The reaction using PCv_3 gave homoallylic alcohol 3aa with high regio- and stereoselectivities in good yield as the sole product (entry 4, Table 1). With bulkier ligands, such as $P(t-Bu)_3$ and XPhos, the three-component coupling reaction did not proceed at all (entries 5 and 6, Table 1). Bidentate phosphine and N-heterocyclic carbene (NHC) ligands were not effective for the coupling reaction and the starting material was recovered quantitatively (entries 7-10, Table 1).

 Table 1
 Ni-Catalyzed Coupling Reaction of Allylbenzene, CO₂, and Me₃Al^a

Ph 1a	+ CO ₂ cat. Ni(cod) ₂ /ligand (1 atm) Me ₃ Al	Ph Me Me Me Me Me Me Me
Entry	Ligand (mmol)	Yield (%, 3aa/4aa) ^b
1	PPh ₃ (0.1)	0
2	P(<i>n</i> -Bu) ₃ (0.1)	27 (94:6)
3	PCyp ₃ (0.1)	37 (95:5)
4	PCy ₃ (0.1)	73 (99:1)
5°	P(<i>t</i> -Bu) ₃ (0.1)	0
6	XPhos (0.1)	0
7	dCype (0.05)	0
8 ^d	IDM (0.05)	0
9 ^d	ICy (0.05)	0
10 ^d	IMes (0.05)	0

^a Conditions: The reaction was conducted using Ni(cod)₂ (0.05 mmol),

ligand (0.05–0.1 mmol), allylbenzene (0.5 mmol), and trimethylaluminum (1.5 mmol; 1 M solution in *n*-hexane) in solvent (4 mL) at 40 °C for 24 h under carbon dioxide (1 atm).

^b E Stereoisomers were formed

 $^{\rm c}$ P(t-Bu)_3 was generated in situ from P(t-Bu)_3-HBF_4 (0.1 mmol) and NEt(i-Pr)_2 (0.1 mmol).

^a NHC ligands were generated in situ from the HCl salts (0.05 mmol) and KOt-Bu (0.05 mmol).

Various 1-alkenes were examined in the coupling reaction under similar conditions. The results are summarized in Table 2. The 2-methyl-, 4-methyl-, 4-methoxy-, and 4fluoro-substituted allylbenzenes gave the corresponding products in good yields and with high regio- and stereoselectivities (entries 1–4, Table 2). With other aryl terminal Cluster

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alkenes, namely 1-allylnaphthalene and 3-allylindole, the desired coupling reaction proceeded to give the homoallylic alcohols in moderate to high yields (entries 5 and 6, Table 2). Simple terminal alkenes such as 1-octene could be used in the coupling reaction and led to high regio- and stereose-lectivities (entry 7, Table 2). Reactions with 4-phenyl-1-butene, 5-hexen-1-ol, and methyl 5-hexenoate gave the corresponding products in moderate yields (entries 8–10, Table 2). With 3,3-diphenyl-1-propene, the three-component coupling reaction proceeded to afford the homoallylic alcohol in a low yield (entry 11, Table 2). The reaction with 4-(4-*tert*-butyl)phenyl-3-methyl-1-butene gave the desired coupling product as a mixture of stereoisomers in a 4:1 ratio (entry 12, Table 2).

IdDie Z NI-Catalyzed Coudling Reaction of Alkenes, CO ₂ , and Me ₂ A	Table 2	Ni-Catalvzed Coupling Read	ction of Alkenes. C	O ₂ , and Me ₂ Al ^a
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R^{1} 1	+ CO ₂ (1 atm)	cat. Ni(cod) ₂ /PCy ₃	H ² Me Me 3
Entry	R ¹	1 R ²	Yield of 3 (%) ^b
1	2-MeC ₆ H ₄	1b H	3ba 64
2	$4-MeC_6H_4$	1c H	3ca 68
3	$4-MeOC_6H_4$	1d H	3da 70
4	$4-FC_6H_4$	1e H	3ea 77
5	1-naphthyl	1f H	3fa 54
6 ^c	3-indolyl	1g H	3ga 86
7	$CH_3(CH_2)_4$	1h H	3ha 54
8	$Ph(CH_2)_2$	1i H	3ia 42
9 ^c	$HO(CH_2)_3$	1j H	3ja 30
10	MeO ₂ C(CH ₂)	з 1k Н	3ka 24
11	Ph	11 Ph	3la 25
12	4-t-BuPhCH ₂	1m Me	3ma 49 ^d

^a Reaction conditions: The reaction was conducted using Ni(cod)₂

(0.05 mmol), PCy_3 (0.1 mmol), alkene (0.5 mmol), and trimethylaluminum (1.5 mmol; 1 M solution in *n*-hexane) in 1,4-dioxane (4 mL) at 40 °C for 24 h under carbon dioxide (1 atm).

^b Only *E* stereoisomer was formed.

^c 2.0 mmol of trimethylaluminum was used.

 $^{d}E/Z = 4:1$. Stereochemistry was determined by NOE experimental analysis.

Next, various organoaluminum reagents were investigated under the same conditions. The results are summarized in Table 3. Other organometallic reagents such as Me-Li, MeMgBr, Me₂Zn, and Me₃B did not react to provide the expected homoallylic alcohols at all. Although Me₃Al promoted the desired reaction to afford homoallylic alcohol **3aa** in good yield and with high regio- and stereoselectivities (entry 1, Table 3), reactions using (CH₂CHCH₂)Et₂Al and (PhCH₂)Et₂Al did not provide the products at all; instead, triallylmethanol **5b** and tribenzylmethanol **5c** were produced (entries 2 and 3, Table 3). Even in the absence of Ni(cod)₂ and PCy₃, **5b** and **5c** were formed. Therefore, it was с

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concluded that the combination of the Ni catalyst and Me₃Al would be enough to accomplish the coupling reaction with alkenes under carbon dioxide (entries 4 and 5, Table 3).

Table 3	Ni-Catalyzed Coupling Reaction of Allylbenzene, CO ₂ , and
Various C	Organoaluminum Reagents ^a

Ph 1a	+ CO ₂ (1 atm) (1 atm) cat. Ni(cod) ₂ /PCy ₃ R ₃ Al or REt ₂ Al	Ph R R R R OH R S
Entry	Organoaluminum 2	Yield of 3^{b} or 5 (%)
1	2a Me ₃ Al	3aa 73
2 ^c	2b (CH ₂ CHCH ₂)Et ₂ Al	5b 51 R = CH ₂ CHCH ₂
3°	2c (PhCH ₂)Et ₂ Al	5c 34 R = Bn
4 ^{c,d}	2b (CH ₂ CHCH ₂)Et ₂ Al	5b 51 R = CH ₂ CHCH ₂
5 ^{c,d}	2c (PhCH ₂)Et ₂ Al	5c 35 R = Bn

^a Conditions: The reaction was conducted using Ni(cod)₂ (0.05 mmol), PCy₃ (0.1 mmol), alkene (0.5 mmol), and organoaluminum reagent (1.5 mmol) in 1,4-dioxane (4 mL) at 40 °C for 24 h under carbon dioxide (1 atm). ^b Only *E* stereoisomer was formed.

^c Organoaluminum reagents **2b** and **2c** were prepared from Et₂AlCl (1 M solution in hexanes) and (CH₂CHCH₂)MgBr (1 M solution in diethyl ether) and PhCH₂MgBr (0.9 M solution in THF), respectively.

^d The reaction was conducted without Ni(cod)₂ and PCy₃.

In order to consider the reaction mechanism, the direct conversions of cinnamyl moieties to homoallylic alcohol 3aa were examined, and the results are displayed in Scheme 3. First, trans-4-phenyl-3-butenoic acid was used as a substrate in the presence of catalytic amounts of Ni(cod)₂ and PCy₃ and excess Me₃Al. However, desired homoallylic alcohol 3aa was not obtained. Next, we investigated the reaction using acetone as the enophile instead of carbon dioxide. The direct coupling of allylbenzene with acetone produced desired homoallylic alcohol 3aa with the *E* configuration in 52% yield as a single isomer.¹⁰ However, in the absence of the Ni catalyst, this coupling reaction did not proceed at all. Thus, the Ni catalyst is indispensable in these carbonyl-ene-type reactions for the formation of homoallylic alcohols from terminal alkenes. We attempted to confirm the formation of an allylic anion from cinnamyl chloride in the presence of Ni(cod)₂, PCy₃, and Me₃Al, but the expected coupling reaction with carbon dioxide was unsuccessful.¹¹ According to these results, it seems doubtful that an allylic anion species is formed in situ to react with acetone to afford desired homoallylic alcohol 3aa.12

Based on our results for the formation of homoallylic alcohols, a possible reaction mechanism for the coupling reaction was proposed and is shown in Scheme 4. First, carbon dioxide reacts with Me₃Al to give acetone in situ,¹³ and then the alkene coordinates with Ni(0) in such a way that minimizes steric repulsion through **I**. Acetone also coordi-

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Scheme 3 Alternative strategies for the Ni-catalyzed formation of homoallylic alcohol **3aa**

nates with the nickel metal center, leading to the formation of five-membered oxanickelacycle intermediate **II**. Here, Me₃Al serves as a Lewis acid, activating acetone and promoting the oxidative cyclization.¹⁴ The phosphine ligand, PCy₃, enhances the Ni complex, accelerating β -hydride elimination, which generates the C=C double bond (**IV**).¹⁵ Finally, transmetalation with Me₃Al occurs via σ -bond metathesis, and this is followed by evolution of methane and regeneration of the Ni(0) active species through reductive elimination. After the hydrolysis of **VI**, the expected homoallylic alcohol, **3**, with the *E* configuration is obtained.

In conclusion, we have developed the Ni-catalyzed multicomponent coupling reaction of simple alkenes, carbon dioxide, and Me₃Al that affords homoallylic alcohols with high regio- and stereoselectivities.¹⁶ Because a ketone is





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generated from carbon dioxide using an organoaluminum reagent, these coupling reactions can be regarded as formal carbonyl-ene-type reactions via oxanickelacycle intermediates. It is considered that the activation of the simple alkenes and carbon dioxide is the driving force behind this carbonyl-ene-type reaction, which will be an important synthetic tool for C–C bond formation.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591845.

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- (16) General Procedure for the Ni-Catalyzed Three-Component Coupling Reaction of Alkene, CO₂, Organoaluminum Reagent (Table 1, Entry 4)

The reaction was undertaken as follows: Into a carbon dioxide purged flask with Ni(cod)₂ (13.8 mg, 0.05 mmol) and PCy₃ (28.1 mg, 0.1 mmol) were introduced successively 1,4-dioxane (4 mL), allylbenzene (59.1 mg, 0.5 mmol), and Me₃Al (1.5 mL of 1 M solution in *n*-hexane, 1.5 mmol) via syringe. The homogeneous mixture was stirred at 40 °C for 24 h, during which the reaction was monitored by TLC. Then the mixture was quenched by adding 2 N HCl (10 mL) and extracted with ethyl acetate three times. The combined organic extracts were washed with brine and then dried (MgSO₄) and concentrated in

vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 2:1, v/v) to give **3aa** (64.3 mg, 0.36 mmol, 73%) as a pale yellow oil.

(E)-2-Methyl-5-phenylpent-4-en-2-ol (3aa)

TLC: R_f = 0.25 (hexane/ethyl acetate = 4:1, v/v). IR (neat): 3387 (m), 3059 (m), 2970 (s), 1599 (s), 1497 (m), 1377 (s), 1140 (s), 968 (s), 692 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 1.27 (s, 6 H), 1.54 (br, 1 H), 2.39 (d, *J* = 7.6 Hz, 2 H), 6.28 (dt, *J* = 15.9, 7.6 Hz, 1 H), 6.46 (d, *J* = 15.9 Hz, 1 H), 7.21 (t, *J* = 7.3 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 2 H), 7.34 (d, *J* = 7.3 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ = 29.3, 47.4, 70.9, 125.7, 126.1, 127.2, 128.5, 133.6, 137.3. HRMS: *m/z* calcd for C₁₂H₁₆O: 176.1201; found: *m/z* (relative intensity) = 176.1203 (9) [M⁺], 118 (100).

(E)-2-Methyldec-4-en-2-ol (3ha)

Pale yellow oil; yield 46.0 mg (0.27 mmol, 54%); TLC: $R_f = 0.50$ (hexane/ethyl acetate = 4:1, v/v). IR (neat): 3361 (br), 2962 (s), 2927 (s), 2856 (m), 1497 (w), 1377 (w), 1151 (w), 972 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 3 H), 1.20 (s, 6 H), 1.26–1.41 (m, 6 H), 1.50 (br, 1 H), 2.03 (q, J = 7.3 Hz, 2 H), 2.16 (d, J = 6.8 Hz, 2 H), 5.46 (dt, J = 15.1, 7.3 Hz, 1 H), 5.53 (dt, J = 15.1, 6.8 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.0$, 22.5, 29.0, 29.2, 31.4, 32.7, 47.0, 70.4, 125.2, 135.4. HRMS: m/z calcd for C₁₁H₂₂O: 170.1671; found: m/z (relative intensity) = 170.1668 (14) [M⁺], 155 (100).