

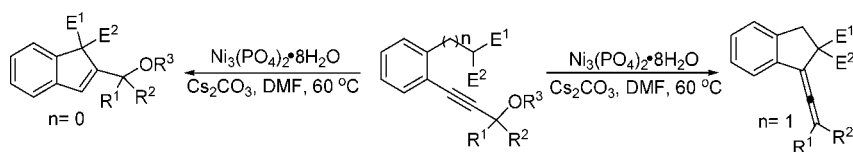
New Insight into Ni(II)-Catalyzed Cyclization Reactions of Propargylic Compounds with Soft Nucleophiles: Novel Indenes Formation

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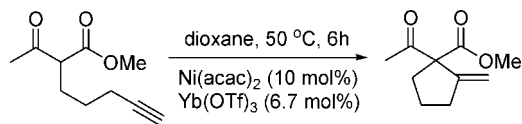
We have disclosed a very nice advance of nickel(II)-catalyzed carboannulation reactions. Highly substituted indene derivatives are readily prepared in moderate to excellent yields under very mild reaction conditions in air via a nickel(II)-catalyzed cyclization of propargylic compounds with soft nucleophiles.

Introduction

Transition metal-catalyzed annulation processes have proven very useful in organic synthesis.¹ Palladium-catalyzed reactions of propargylic compounds with soft nucleophiles serve as a useful method for the construction of carbon–carbon and carbon–heteroatom bonds.² However, most of the work in this field has been devoted to relatively expensive and air-sensitive palladium catalysts and special ligands, limiting their application at least in large-scale preparation. Catalysis in the presence of inexpensive and nontoxic metals has gained increasing attention in chemical research within the past years.³

The cyclizations mediated by inexpensive nickel complexes have been extensively explored in recent years for substrates such as dienes, enynes, dienynes, and bis-dienes.⁴ To the best of our knowledge, nickel-catalyzed reactions with soft nucleophiles, compared with the well-established palladium-catalyzed reactions, generally are considered as less efficient⁵ and were scarcely studied and have almost essentially been used with hard nucleophiles such as organometallic reagents.⁶ Furthermore, in contrast to the extensive studies on nickel-catalyzed reactions of allylic compounds, studies on the analogous reactions of propargylic compounds were initiated much later and were less extensive.

SCHEME 1



Recently, Yang and co-workers reported a Ni(II)-catalyzed Conia-ene reaction of 1,3-dicarbonyl compounds with alkynes.⁷ In the presence of Ni(acac)₂ and Yb(OTf)₃, various acetylenic 1,3-dicarbonyl compounds underwent Conia-ene reaction to give mono- and bicyclic olefinic cyclopentanes (Scheme 1). In²

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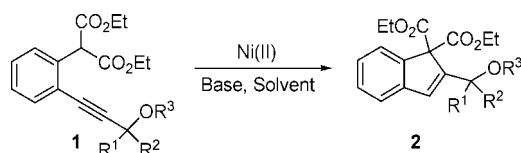
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SCHEME 2



connection with our ongoing projects on the cyclization reactions via transition metal-catalysis,⁸ we expected to investigate the extension of the methodology to pursue an inexpensive and mild procedure for the convenient synthesis of various functionalized indene derivatives. Herein, we wish to report an application of Ni(II) catalysts to a homogeneous cyclization reaction of propargylic compounds with soft nucleophiles (Scheme 2).

Results and Discussion

Synthesis of Functionalized Indenes by the Nickel(II)-Catalyzed Cyclization Reaction of Propargylic Compounds. In our initial study, we focused on finding the optimal reaction conditions for the cyclization step. The reaction was first attempted using 1.0 equiv of 3-(2-(diethoxycarbonyl)methyl)-phenylprop-2-ynyl ethyl carbonate (**1a**, 0.2 mmol), 5 mol % of Ni(dppf)Cl₂ and 2.0 equiv of K₂CO₃ in DMF at 60 °C for 3 h in air. The desired product **2a** was formed in 79% isolated yield (Table 1, entry 1). Cs₂CO₃ and K₃PO₄ were investigated as bases, Cs₂CO₃ provided a good yield and short time (entries 2–3). Other solvents such as CH₃CN and THF were less or no effective (entries 4–5). The catalytic efficiency of various nickel catalysts has also been studied (entries 6–13). But none of them gave a higher yield than Ni₃(PO₄)₂·8H₂O. The amount of nickel catalysts was examined as well (entries 14–15). We found that 2 mol% of Ni₃(PO₄)₂·8H₂O also afforded product in an excellent yield and reproducibility, although a longer reaction time was needed. Moreover, it should be pointed out that all reactions were carried out in open air without exclusion of oxygen from the reaction flask. The optimum reaction conditions thus far developed employ 1.0 equiv of **1a**, 2.0 equiv of Cs₂CO₃, and 2 mol% Ni₃(PO₄)₂·8H₂O in DMF at 60 °C in air.

Under the optimized reaction conditions above, the breadth and scope for this methodology were investigated next. The reactions of different substituted propargylic compounds were investigated first and the results are summarized in Table 2. The reactions of propargylic carbonate **1b** and propargylic acetate **1c** also gave the desired products **2b** and **2c** in excellent yields (Table 2, entries 2–3). A good yield of the expected product has been obtained by using substituted secondary carbonate, having methyl substituted **1d** (entry 4). Nevertheless, phenyl substituted secondary carbonate **1e** gave a complex mixture of unidentified products (entry 5). No reaction was observed when the reaction was carried out by using tertiary propargylic carbonate **1f** (entry 6). This is probably due to the steric hindrance, the more substituted end being now too crowded.

We considered intramolecular nucleophiles containing heteroatoms particularly attractive, since they have special nucleophilicity

TABLE 1. Optimization of the Ni(II)-Catalyzed Cyclization of Propargylic Carbonate **1a**^a

entry	catalyst	base	solvent	Ni(mol %)	t (h)	yield(%) ^b
1	Ni(dppf)Cl ₂	K ₂ CO ₃	DMF	5	3	79
2	Ni(dppf)Cl ₂	Cs ₂ CO ₃	DMF	5	2	83
3	Ni(dppf)Cl ₂	K ₃ PO ₄	DMF	5	6	65
4	Ni(dppf)Cl ₂	Cs ₂ CO ₃	CH ₃ CN	5	2	80
5	Ni(dppf)Cl ₂	Cs ₂ CO ₃	THF	5	6	n.r.
6	Ni(dppe)Cl ₂	Cs ₂ CO ₃	DMF	5	2	85
7	Ni(dppb)Cl ₂	Cs ₂ CO ₃	DMF	5	3	77
8	Ni(PPh ₃) ₂ Cl ₂	Cs ₂ CO ₃	DMF	5	3	74
9	Ni(acac) ₂	Cs ₂ CO ₃	DMF	5	6	82
10	NiCl ₂ ·6H ₂ O	Cs ₂ CO ₃	DMF	5	12	61
11	Ni(OAc) ₂ ·4H ₂ O	Cs ₂ CO ₃	DMF	5	12	69
12	Ni(OH) ₂ ·H ₂ O	Cs ₂ CO ₃	DMF	5	1	86
13	Ni ₃ (PO ₄) ₂ ·8H ₂ O	Cs ₂ CO ₃	DMF	5	1	91
14	Ni ₃ (PO ₄) ₂ ·8H ₂ O	Cs ₂ CO ₃	DMF	2	3	91
15	Ni ₃ (PO ₄) ₂ ·8H ₂ O	Cs ₂ CO ₃	DMF	1	6	83

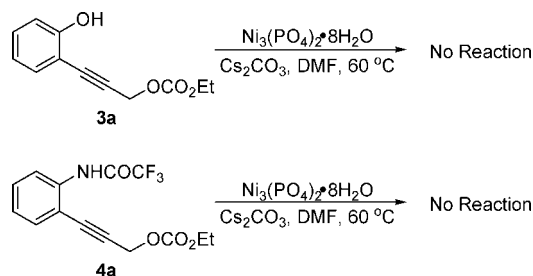
^a Reactions were carried out on a 0.2 mmol scale in 2.0 mL of solvent at 60 °C in air for the specified period of time with 1.0 equiv of **1a**, 2.0 equiv of base, and [Ni]. ^b Isolated yields.

TABLE 2. Nickel(II)-Catalyzed Cyclization of Propargylic Esters **1**^a

entry	1	t (h)	2	yield (%) ^b
1	R ¹ = H, R ² = H, R ³ = CO ₂ Et (1a)	3	2a	91
2	R ¹ = H, R ² = H, R ³ = CO ₂ Me (1b)	1	2b	88
3	R ¹ = H, R ² = H, R ³ = Ac (1c)	3	2c	85
4	R ¹ = Me, R ² = H, R ³ = CO ₂ Et (1d)	1	2d	79
5	R ¹ = Ph, R ² = H, R ³ = CO ₂ Me (1e)	1	mixture	—
6	R ¹ = Me, R ² = Me, R ³ = CO ₂ Me (1f)	6	—	n.r. ^c

^a Condition: **1** (0.2 mmol), Cs₂CO₃ (2.0 equiv) and 2 mol% Ni₃(PO₄)₂·8H₂O in DMF (2.0 mL) at 60 °C in air. ^b Isolated yields. ^c n.r. = no reaction.

SCHEME 3



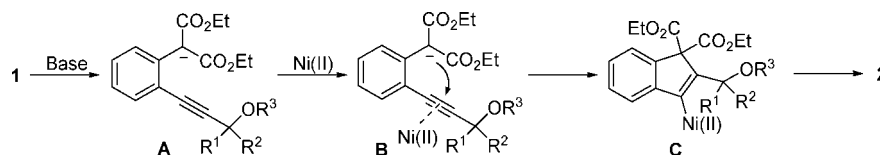
and probably allowed for various heterocycles. Although no reaction was observed when ethyl 3-(2-hydroxyphenyl)-prop-2-ynyl carbonate (**3a**) and 3-(2-(2,2,2-trifluoroacetamido)phenyl)prop-2-ynyl ethyl carbonate (**4a**) were conducted

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SCHEME 4

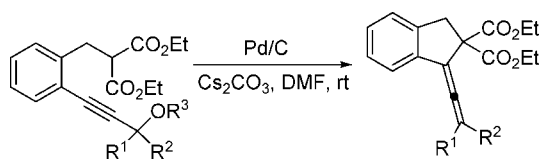


under the above optimized reaction conditions. Further raising the reaction temperature, loading the amount of catalyst to 10% $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and using stronger bases exhibit no effect (Scheme 3).

On the basis of our knowledge of the transition metal-catalyzed carboannulation of alkynes,^{7,9} combined with our observed experiment features, a plausible mechanism is proposed in Scheme 4; it consists of the following key steps: (a) generation of a carbanion **A** by the base; (b) coordination of the Ni(II) specie to the alkyne triple bond affords the alkynynickel complex **B**; and (c) intramolecular nucleophilic attack of the carbanion on the activated triple bond to afford a Ni(II) vinyl specie **C** and then protonation of the C–Ni bond to give the cyclization product **2**.

Synthesis of Allenyl Indenes by the Nickel(II)-Catalyzed Cyclization Reaction of Propargylic Compounds. Allenes are regarded as useful building blocks for organic synthesis¹⁰ and the development of versatile methods for the preparation of allenes has been of great importance.¹¹ Allenes can be generally prepared from propargylic derivatives by $\text{S}_{\text{N}}2'$ -type displacement with organocopper species.¹² Methodologies to the synthesis of allenes via nickel-catalyzed, such as carbonylation of propargylic and allenyl halides,¹³ reactions of propargylic compounds with Grignard reagents or other organometallic reagents,¹⁴ are generally driven by Ni(0) species. Up to now, there is no report about carboannulation of propargylic compounds driven by nickel(II) species for the preparation of allene derivatives.

SCHEME 5



Recently, we have developed an efficient route to allenyl indenenes by the Pd/C-catalyzed carboannulation of propargylic compounds^{8e,f} (Scheme 5). These successful results encouraged us to extend this nickel(II)-mediated methodology to the synthesis of allenyl indenenes. Herein, we report the full details of this synthesis of allenyl indenenes.

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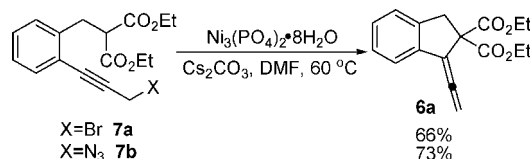
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Initially, we started out the reaction of 3-(2-(2,2-di(ethoxycarbonyl)ethyl)phenyl)prop-2-ynyl ethyl carbonate (**5a**) under the optimized reaction conditions above. Satisfactorily, the allenyl indene product **6a** was isolated in 83% yield as a single product (Table 2, entry 1).

The general applicability of the reaction of primary, substituted secondary and tertiary propargylic esters was investigated next. The reactions of propargylic acetate **5b** and propargylic phosphate **5c** gave the desired product **6a** in good yields under the optimized reaction conditions above (Table 3, entries 2–3). Secondary carbonates possessing various substituents (alkyl-, heterocyclic-, and aryl- substituted) at the propargylic position also worked well, and afforded the corresponding products in moderate yields (entries 4–13). Functional groups, such as methyl, chloro, bromo, and methoxyl, etc., were well tolerated in the reactions. Meanwhile, the reactions of tertiary propargylic acetates have also been studied. Moderate yields of the expected products have been obtained from **5n**, **5o**, and **5p** (entries 14–16).

Propargylic alcohols were also investigated under the optimized reaction conditions. Propargylic alcohol **5q** furnished a 56% yield of the desired allenyl indene **6a** in 5 h (Table 3, entry 17). Propargylic alcohols with different electron-withdrawing groups were subjected to the reaction, such as β -ketoester **5r** led to a 49% yield of product **6o** and shorter reaction time was required (entry 18). The reactivity of substituted secondary and tertiary propargylic alcohols have also been examined. Expectedly, longer reaction times were needed and lower yields were obtained (entries 19–20). Compared with the reaction of propargylic esters, the reactivity of propargylic alcohols were comparatively a little lower, because the hydroxy is not a good leaving group and products **6** are very sensitive and could not be stored for extended periods. Furthermore, additional attempts to extend substrates to propargylic ethers were unsuccessful.

SCHEME 6



To further probe our Ni(II)-catalyzed carboannulation reactions, the propargylic compounds with different leaving groups has also been examined (Scheme 6). Gratifyingly, the desired product **6a** was isolated in 66 and 73% yields, and it was observed that the yields of the reactions employing propargyl bromide **7a** and propargyl azide **7b** are generally higher than those utilizing propargylic alcohols.

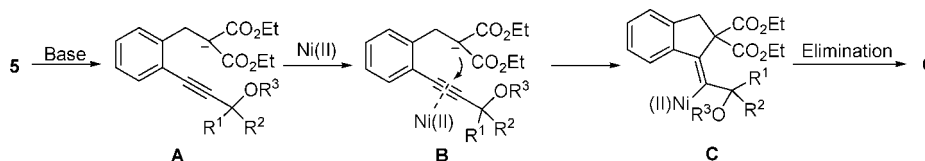
The formation of these allenyl indenenes can be explained by the following processes (Scheme 7). It consists of the following key steps: (a) generation of a carbanion **A** by the base; (b) coordination of the Ni(II) specie to the alkyne triple bond affords the alkynynickel complex **B**, which activates the triple bond

TABLE 3. Nickel(II)-Catalyzed Cyclization of Propargylic Compounds **5**^a

entry	5	t(h)	6	yield (%) ^b
1	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = H, R ³ = CO ₂ Et (5a)	1	6a	83
2	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = H, R ³ = Ac (5b)	3	6a	75
3	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = H, R ³ = PO(OEt) ₂ (5c)	1	6a	81
4	E ¹ = E ² = CO ₂ Et, R ¹ = Me, R ² = H, R ³ = CO ₂ Et (5d)	2	6b	78
5	E ¹ = E ² = CO ₂ Et, R ¹ = Ph, R ² = H, R ³ = CO ₂ Et (5e)	2	6c	75
6	E ¹ = E ² = CO ₂ Et, R ¹ = <i>m</i> -tol, R ² = H, R ³ = CO ₂ Et (5f)	3	6d	70
7	E ¹ = E ² = CO ₂ Et, R ¹ = <i>o</i> -ClC ₆ H ₄ , R ² = H, R ³ = CO ₂ Et (5g)	3	6e	65
8	E ¹ = E ² = CO ₂ Et, R ¹ = 2,4-diClC ₆ H ₃ , R ² = H, R ³ = CO ₂ Et (5h)	4	6f	68
9	E ¹ = E ² = CO ₂ Et, R ¹ = <i>o</i> -BrC ₆ H ₄ , R ² = H, R ³ = CO ₂ Et (5i)	3	6g	73
10	E ¹ = E ² = CO ₂ Et, R ¹ = <i>o</i> -MeOC ₆ H ₄ , R ² = H, R ³ = CO ₂ Et (5j)	4	6h	69
11	E ¹ = E ² = CO ₂ Et, R ¹ = , R ² = H, R ³ = CO ₂ Et (5k)	4	6i	61
12	E ¹ = E ² = CO ₂ Et, R ¹ = 1-naphthyl, R ² = H, R ³ = CO ₂ Et (5l)	3	6j	74
13	E ¹ = E ² = CO ₂ Et, R ¹ = 2-furyl, R ² = H, R ³ = CO ₂ Et (5m)	3	6k	66
14	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = Me, R ³ = Ac (5n)	4	6l	63
15	E ¹ = E ² = CO ₂ Et, R ¹ = Ph, R ² = Me, R ³ = Ac (5o)	5	6m	55
16	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = Ph, R ³ = Ac (5p)	5	6n	52
17	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = R ³ = H (5q)	5	6a	56
18	E ¹ = COCH ₃ , E ² = CO ₂ Et, R ¹ = R ² = R ³ = H (5r)	3	6o	49
19	E ¹ = E ² = CO ₂ Et, R ¹ = Me, R ² = R ³ = H (5s)	6	6b	52
20	E ¹ = E ² = CO ₂ Et, R ¹ = R ² = Me, R ³ = H (5t)	6	6l	45

^a Condition: **5** (0.2 mmol), Cs₂CO₃ (2.0 equiv) and 2 mol% Ni₃(PO₄)₂·8H₂O in DMF (2.0 mL) at 60 °C in air. ^b Isolated yields.

SCHEME 7



toward nucleophilic attack; and (c) intramolecular nucleophilic attack of the carbanion on the activated triple bond to afford a Ni(II) vinyl specie **C** and then undergoes α -heteroatom elimination (α -oxygen elimination) to afford the cyclization product **6**. The reaction appears to be related to an S_N2'-type displacement of a leaving group by an intramolecular nucleophile.

Conclusions

In conclusion, we have developed a novel, direct route to highly substituted indene derivatives via Ni(II)-catalyzed cy-

clization. Meanwhile, our research has disclosed a very nice advance of nickel-catalyzed carboannulation reactions of propargylic compounds under very mild conditions in air. It is worth noting that no expensive catalyst and special ligand are required for the reaction.

Experimental Section

General Procedure for the Preparation of Indene Derivatives **2.** To a solution of propargylic esters **1** (0.20 mmol) in DMF (2.0 mL) was added Cs₂CO₃ (130.5 mg, 0.4 mmol). The

mixture was stirred for 1 min and $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (2.0 mg, 0.004 mmol, 2 mol %) was added. The resulting mixture was then stirred at 60 °C in air. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was allowed to cool to room temperature and quenched with water, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford indene derivatives **2**.

(1,1-Di(Ethoxycarbonyl)-1*H*-inden-2-yl)methyl Ethyl Carbonate (2a). Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.67–7.64 (d, J = 6.9 Hz, 1H), 7.32–7.23 (m, 3H), 6.97 (s, 1H), 5.20 (s, 2H), 4.26–4.19 (m, 6H), 1.34–1.23 (m, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.2, 154.9, 142.8, 140.5, 140.0, 133.8, 128.7, 126.4, 125.2, 121.6, 70.6, 64.3, 64.0, 62.3, 14.2, 13.8; IR (neat, cm^{-1}) 1742, 1465, 1261, 1046, 860, 755; Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_7$: C 62.97; H 6.12. Found: C 62.85; H 6.30.

General Procedure for the Preparation of Allenyl Indene Derivatives 6. To a solution of propargylic compounds **5** or **7** (0.20 mmol) in DMF (2.0 mL) was added Cs_2CO_3 (130.5 mg, 0.4 mmol). The mixture was stirred for 1 min, and $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (2.0 mg, 0.004 mmol, 2 mol %) was added. The resulting mixture was then stirred at 60 °C in air. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was allowed

to cool to room temperature and quenched with water, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford indene derivatives **6**.

Diethyl 1-(2-*m*-Tolylvinylidene)-1*H*-indene-2,2(3*H*)-dicarboxylate (6d). Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.21–7.08 (m, 7H), 6.96–6.95 (m, 1H), 6.69 (s, 1H), 4.17–3.94 (m, 4H), 3.79–3.62 (q, J = 17.1 Hz, 2H), 2.23 (s, 3H), 1.19–1.10 (m, 3H), 1.03–0.98 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.2, 169.9, 140.1, 138.1, 136.4, 133.3, 128.5, 128.4, 128.0, 127.4, 124.7, 124.6, 122.7, 111.1, 101.9, 62.7, 62.1, 61.9, 39.7, 21.3, 14.1, 13.8; IR (neat, cm^{-1}) 1729, 1251, 1181, 1057, 908, 733; Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4$: C 76.57; H 6.43. Found: C 76.45; H 6.36.

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Supporting Information Available: Typical experimental procedure and characterization data for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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