# Rhodium Complex-Catalyzed Desilylative Cyclocarbonylation of 1-Aryl-2-(trimethylsilyl)acetylenes: A New Route to 2,3-Dihydro-1*H*-inden-1-ones

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Under water gas shift reaction conditions, 1-aryl-2-(trimethylsilyl)acetylenes undergo Rh-catalyzed desilylative cyclocarbonylation to give 2,3-dihydro-1*H*-inden-1-ones and trimethylsilanol. A wide variety of functional groups, such as methoxy, chloro, acetyl, ethoxycarbonyl, cyano, and trifluoromethyl, are tolerated on the aromatic ring under the reaction conditions. The products were obtained in good to excellent yield whether the substituent on the aromatic ring was electron-donating or electron-withdrawing. The cyclizations of substrates bearing a meta substituent on the aromatic ring regiospecifically gave 5-substituted-2,3-dihydro-1*H*-inden-1-ones except when the meta substituent was a methoxy group. The desilylative cyclocarbonylation is an alternative to the conventional preparation of 2,3-dihydro-1*H*-inden-1-ones, an intramolecular Friedel–Crafts acylation. A possible mechanism for the process is described.

## Introduction

Transition metal complex-catalyzed carbonylation has been proven to be a useful method for the direct introduction of a carbonyl group into an organic molecule via the insertion of carbon monoxide into a carbon–metal bond.[1] An important variant of carbonylation is cyclocarbonylation.[2] Because cyclocarbonylation allows the introduction of a carbonyl group along with ring closure, the reaction is expected to provide a novel tool for the construction of cyclic systems. In fact, intramolecular dehydrohalogenative carbonylation of organic halides has been successfully applied to the synthesis of β-lactams[2b-f] and lactones.[2g,h] Recently, another version of the cyclocarbonylation involving C–H activation of an aromatic ring has received much attention.[3]

The long history of carbonylation of acetylenes began with Reppe's $Ni(CO)_4$-catalyzed synthesis of acrylic acid from acetylene.[4] A number of synthetic applications and mechanistic studies have been reported.[5] However, cyclocarbonylation of acetylenes involving C–H activation of an aromatic ring has rarely been explored. Takahashi and co-workers recently reported that the $Co_2(CO)_8$-catalyzed cyclocarbonylation of diarylacetylenes gave 2-aryl-3-hydro-1*H*-inden-1-ones.[6] This cyclocarbonylation has limitation: aryl groups on both acetylenic carbons are necessary for a good yield of the product. The reaction of 1-phenyl-1-propyne gave 2-methyl-3-hydro-1*H*-inden-1-one in 17% yield.

We previously reported the stereodefined synthesis of [(*E*)-β-(ethoxycarbonyl)vinyl]silane by Pd(II)-catalyzed hydroesterification of silylacetylenes.[7] In the course of this study, we found a novel cyclocarbonylation of 1-aryl-2-(trimethylsilyl)acetylene involving C–H activation of an aromatic ring; Rh-catalyzed reaction of 1-phenyl-2-(trimethylsilyl)acetylene under water gas shift reaction conditions gave 2,3-dihydro-1*H*-inden-1-one in good yield. We have extended this chemistry to develop a new and general method for the synthesis of 2,3-dihydro-1*H*-inden-1-ones.

## Results and Discussion

1-Phenyl-2-(trimethylsilyl)acetylene (**1a**) was cyclocarbonylated to give 2,3-dihydro-1*H*-inden-1-one (**2a**) (61% yield) and trimethylsilanol in the presence of $Et_3N$ and a catalytic amount of $RhCl(PPh_3)_3$ under water gas shift reaction conditions (eq 1). The reaction in the absence of $H_2O$ gave no product, and the starting material was recovered. Replacement of $H_2O$ by $D_2O$ gave the deuteriated product. That deuterium atoms were incorporated into both of the methylene carbons of **2a** shows that $H_2O$ acts as the hydrogen source. The use of molecular hydrogen in place of $H_2O$ resulted in a poor yield along and in the formation of hydroformylation products (Scheme I). Water gas shift reaction conditions were necessary for good yields of **2a**.

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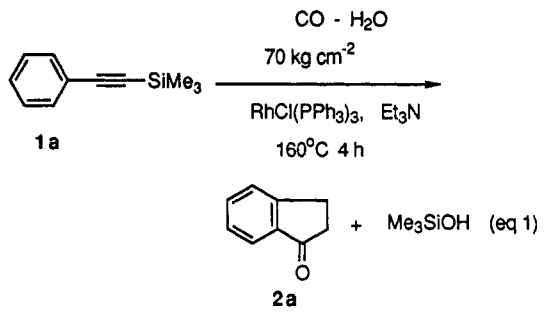
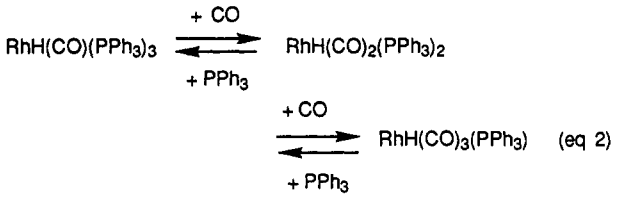



It is well known that bases effectively promote the water gas shift reaction.[8] $Et_3N$ is an effective additive for this cyclocarbonylation; in the absence of $Et_3N$, the reaction gave **2a** in 2% yield.

We turned our attention to improving the yield of **2a** by modifying the ligand on rhodium. We chose $[Rh(COD)Cl]_2$ as the catalyst because the 1,5-cyclooctadiene ligand on the rhodium complex could be replaced easily by the added phosphine ligand to generate a rhodium phosphine species.[9] The results are summarized in Table I. We surveyed several phosphine ligands including a bidentate ligand at P/Rh = 5 and found triphenylphosphine to be the most effective ligand (entry 3). The addition of an excess of triphenylphosphine to $[Rh(COD)Cl]_2$ in the reaction mixture resulted in an increase in the yield of **2a** (entries 10–12).

In contrast to our case, adding a large excess of triphenylphosphine to a metal complex generally suppresses the reaction by blocking the vacant ligand coordination site on the metal required for the incoming substrate. The role of the large excess of triphenylphosphine in our case can reasonably be interpreted in terms of an equilibrium between several rhodium–phosphine species generated in situ, which was studied by Wilkinson and co-workers in connection with the mechanism of the triphenylphosphine-modified rhodium-catalyzed hydroformylation (eq 2).[10] The presence of a large excess of




triphenylphosphine causes the equilibrium to shift to a rhodium species coordinated by a greater number of triphenylphosphines. This rhodium phosphine species is more catalytically active (vide infra), and the yield of **2a** is increased.

After the discovery of the effect of excess triphenylphosphine, we carried out reactions catalyzed by several rhodium complexes combined with large excesses of triphenylphosphine in the presence of $Et_3N$. The results are summarized in Table II. In every case, a good yield of **2a** was obtained. A rhodium cation complex or a rhodium carbonyl cluster gave somewhat lower yields of **2a** compared with the other catalysts (entries 4 and 7).

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**Scheme I**

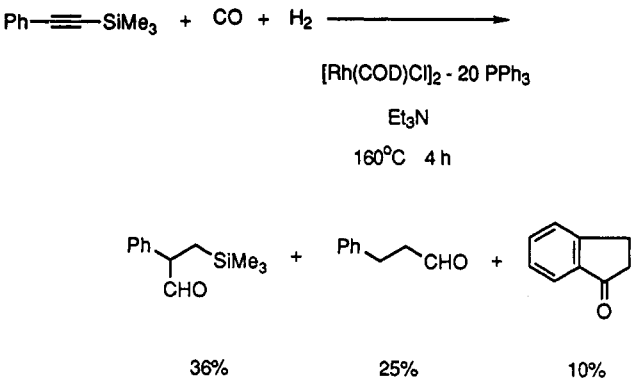



**Table I. The Effect of the Phosphine Ligand on the $[Rh(COD)Cl]_2$-Catalyzed Desilylative Cyclocarbonylation of 1a[a]**

| entry | ligand | P/Rh | conversion of 1a, %[b] | yield of 2a, %[b] |
|---|---|---|---|---|
| 1 | – | 0 | 96 | 25 |
| 2 | $PPh_3$ | 2 | 100 | 60 |
| 3 | $PPh_3$ | 5 | 99 | 67 |
| 4 | $PPh_2Me$ | 5 | 65 | 48 |
| 5 | $AsPh_3$ | 5 | 76 | 21 |
| 6[c] | $P(o\text{-Tol})_3$ | 5 | 97 | 13 |
| 7[d] | dppe | 5 | 85 | 0 |
| 8[e] | dppb | 5 | 78 | 42 |
| 9[f] | dppf | 5 | 97 | 49 |
| 10 | $PPh_3$ | 10 | 100 | 72 |
| 11 | $PPh_3$ | 20 | 99 | 79 |
| 12 | $PPh_3$ | 30 | 100 | 78 |

[a] A mixture of **1a** (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), $[Rh(COD)Cl]_2$ (0.05 mmol), ligand, and THF (10 mL) was stirred at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Determined by GLC. Based on the amount of **1a**. [c] Tri(*o*-tolyl)phosphine. [d] dppe = 1,2-bis(diphenylphosphino)ethane. [e] dppb = 1,4-bis(diphenylphosphino)butane. [f] dppf = 1,1′-bis(diphenylphosphino)ferrocene.

**Table II. Rhodium Complex-Catalyzed Desilylative Cyclocarbonylation of 1a in the Presence of a Large Excess of Triphenylphosphine[a]**

| entry | catalyst system | P/Rh | conversion of 1a, %[b] | yield of 2a, %[b] |
|---|---|---|---|---|
| 1 | $RhH(CO)(PPh_3)_3 + PPh_3$ | 20 | 97 | 73 |
| 2 | $RhCl(PPh_3)_3 + PPh_3$ | 20 | 92 | 74 |
| 3[c] | $[Rh(CO)_2Cl]_2 + PPh_3$ | 20 | 97 | 79 |
| 4 | $[Rh(COD)_2]BF_4 + PPh_3$ | 20 | 96 | 64 |
| 5[c] | $[Rh(OAc)_2]_2 + PPh_3$ | 20 | 67 | 45 |
| 6 | $RhCl_3 \cdot xH_2O + PPh_3$ | 20 | 96 | 82 |
| 7[d] | $Rh_6(CO)_{16} + PPh_3$ | 20 | 98 | 63 |

[a] A mixture of **1a** (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), catalyst (0.1 mmol), $PPh_3$ (2 mmol), and THF (10 mL) was stirred at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Determined by GLC. Based on the amount of **1a**. [c] Catalyst (0.05 mmol). [d] Catalyst (0.017 mmol).

The effects of the reaction temperature and the carbon monoxide pressure on the reaction are summarized in Table III. To obtain **2a** in good yield, the reaction temperature must be higher than 160 °C, and the initial pressure of carbon monoxide must be higher than 40 kg cm$^{-2}$.

As discussed above, $Et_3N$ effectively promoted the reaction. We examined the effect of other amines and inorganic bases on the reaction. The results are summarized in Table IV. $Et_3N$ was the most effective of the amines surveyed. The reaction time was affected by the amount of $Et_3N$ employed as an additive. The reaction in the presence of 2 equiv of $Et_3N$ relative to **1a** was completed in 4 h (entry 1). However, a decrease in the

**Table III. Effect of Reaction Temperature and Carbon Monoxide Pressure[a]**

| entry | reaction temperature, °C | carbon monoxide pressure, kg cm$^{-2}$ | conversion of 1a, %[b] | yield of 2a, %[b] |
|---|---|---|---|---|
| 1 | 190 | 70 | 97 | 79 |
| 2 | 160 | 70 | 99 | 79 |
| 3 | 130 | 70 | 30 | 14 |
| 4 | 160 | 90 | 96 | 71 |
| 5 | 160 | 40 | 85 | 71 |
| 6 | 160 | 20 | 25 | 19 |

[a] A mixture of 1a (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), $[Rh(COD)Cl]_2$ (0.05 mmol), $PPh_3$ (2 mmol), and THF (10 mL) was stirred for 4 h. [b] Determined by GLC. Based on the amount of 1a.

**Table IV. Effect of Additives[a]**

| entry | additive | additive/1a | reaction time, h | conversion of 1a, %[b] | yield of 2a, %[b] |
|---|---|---|---|---|---|
| 1 | $Et_3N$ | 2 | 4 | 99 | 79 |
| 2 | $Et_3N$ | 1 | 7 | 95 | 73 |
| 3 | $Et_3N$ | 0.5 | 16 | 95 | 77 |
| 4 | $Et_2NH$ | 2 | 4 | 96 | 50 |
| 5 | $n$-$BuNH_2$ | 2 | 4 | 100 | 0 |
| 6 | $Me_2N(CH_2)_3NMe_2$ | 2 | 4 | 98 | 73 |
| 7 | pyridine | 2 | 4 | 5 | 3 |
| 8 | NaOAc | 2 | 4 | 98 | 69 |
| 9 | $K_2CO_3$ | 2 | 4 | 95 | 66 |

[a] A mixture of 1a (5 mmol), additive, $H_2O$ (50 mmol), $[Rh(COD)Cl]_2$ (0.05 mmol), $PPh_3$ (2 mmol), and THF (10 mL) was stirred at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Determined by GLC. Based on the amount of 1a.

**Table V. Effect of Solvent[a]**

| entry | solvent | conversion of 1a, %[b] | yield of 2a, %[b] |
|---|---|---|---|
| 1 | THF | 99 | 79 |
| 2 | MeCN | 81 | 24 |
| 3 | EtOH | 98 | 56 |
| 4 | benzene | 52 | 44 |

[a] A mixture of 1a (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), $[Rh(COD)Cl_2$ (0.05 mmol), $PPh_3$ (2 mmol), and solvent (10 mL) was stirred for 4 h at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Determined by GLC. Based on the amount of 1a.

amount of $Et_3N$ resulted in a prolongation of the reaction time (entries 2 and 3). Although inorganic bases were insoluble in the reaction mixture, comparable yields of **2a** were obtained when they were used (entries 8 and 9).

The solvent had a considerable effect on the yield of **2a** (Table V). THF gave a good result (entry 1). The use of other solvents resulted in a decrease in the yield of **2a** whether the reaction mixture was homogeneous or not (entries 2–4).

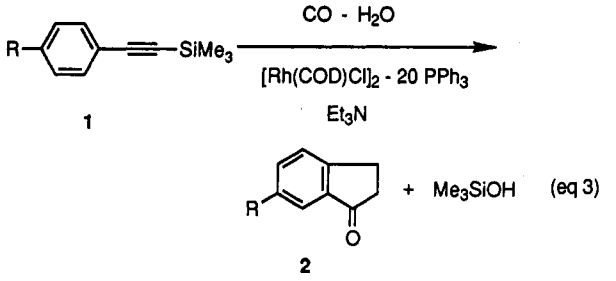
These observations lead to the optimized conditions: a reaction temperature of 160 °C, an initial carbon monoxide pressure of 70 kg cm$^{-2}$, 2 equiv of $Et_3N$ relative to the substrate, a catalytic amount of the rhodium complex, and a large excess of triphenylphosphine relative to the rhodium complex.

Several 1-aryl-2-(trimethylsilyl)acetylenes (**1b–g**) bearing a substituent at the para position on the aromatic ring were subjected to the desilylative cyclocarbonylation under the optimized conditions described above. The effects of the electronic properties of the substituents on the yield and the chemoselectivity of the reaction were examined (eq 3). The results are summarized in Table VI. This desilylative cyclocarbonylation tolerates a considerable range of 1-aryl-2-(trimethylsilyl)acetylenes. The products were obtained in good to excellent yields whether the substituent on the aromatic ring was electron-donating or electron-withdrawing. No significant deactivating effect

**Table VI. Desilylative Cyclocarbonylation of 1[a]**

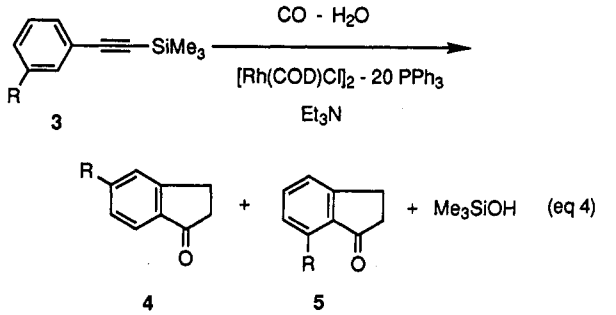
| entry | substrate | R | product | yield of 2, %[b] |
|---|---|---|---|---|
| 1 | **1b** | Me | **2b** | 86 |
| 2 | **1c** | MeO | **2c** | 90 |
| 3 | **1d** | Cl | **2d** | 78 |
| 4 | **1e** | $EtO_2C$ | **2e** | 83 |
| 5 | **1f** | Ac | **2f** | 77 |
| 6 | **1g** | NC | **2g** | 67 |

[a] A mixture of 1 (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), $[Rh(COD)Cl]_2$ (0.05 mmol), $PPh_3$ (2 mmol), and THF (10 mL) was stirred at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Isolated yield.




induced by the electronic properties of the substituent was found. The substrate bearing a cyano group gave a somewhat lower yield than other substrates (entry 6). This desilylative cyclocarbonylation is highly chemoselective, i.e., the reaction is tolerant of a wide variety of functional groups on the aromatic ring. For example, methoxy, chloro, ethoxycarbonyl, cyano, and acetyl group are tolerated in spite of a relatively high reaction temperature. The high chemoselectivity makes the reaction a new method for the construction of a highly functionalized 2,3-dihydro-1*H*-inden-1-ones that doesn't require functional group interconversions or protections and deprotections.

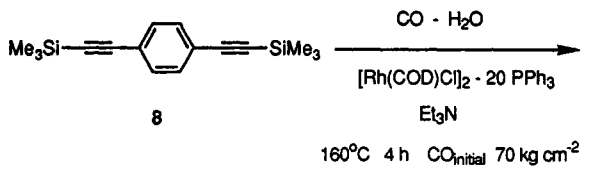
Two isomeric products (**4** and **5**) can be obtained from the carbonylation of silylacetylene **3** (eq 4). To determine




the selectivity of the reaction, we subjected several substrates to the reaction conditions. The results are summarized in Table VII. The products were obtained in good to excellent yields. The reactions gave **4** regiospecifically as a single product except for the reaction of **3b**. The less hindered of the two possible reaction sites was carbonylated selectively.

Substrates bearing a substituent at the ortho position on the aromatic ring gave the corresponding products in good yields (Scheme II). The yields of the products were somewhat lower than those from meta- or para-substituted substrates.

Silylacetylene **8** gave the doubly carbonylated product in excellent yield (eq 5). Compound **9** was obtained as a single product. The other possible isomer, **10**, was not obtained.

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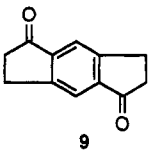
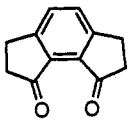


+ 2Me3SiOH (eq 5)

9

Yield 78%

Some derivatives of 2,3-dihydro-1*H*-inden-1-ones are biologically active. Certain Mannich base derivatives have



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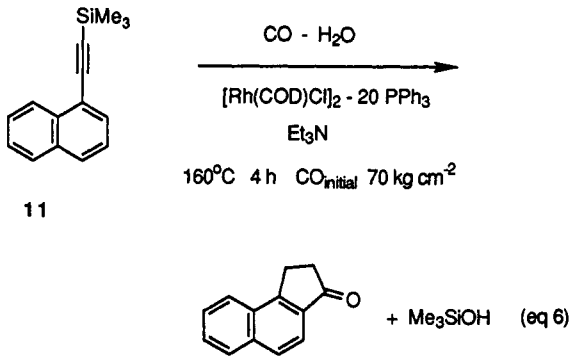
shown antiinflammatory activity.[11] The chrysanthemic esters of indanols show insecticidal activity.[12] Some inden-1-ones are reported to be useful starting materials for the preparation of 2-(arylmethyl)arylacetic acids, which are potential antiinflammatory agents.[13] These biological activities are strongly influenced by the substituents on the inden-1-one nucleus. A method for constructing highly functionalized inden-1-ones is desired.

Generally, intramolecular Friedel–Crafts acylation of 3-arylpropionic acids has been used for the preparation of 2,3-dihydro-1*H*-inden-1-ones.[14] Our cyclocarbonylation has several advantages over the Friedel–Crafts method. First, substrates bearing functional groups such as chloro, acetyl, ethoxycarbonyl, cyano, and trifluoromethyl give the corresponding products in good yields. Second, the cyclizations of substrates bearing a meta substituent on the aromatic ring regiospecifically gave 5-substituted-2,3-dihydro-1*H*-inden-1-ones as single products except when the substituent was a methoxy group. In contrast, the cyclization of 3-(3-methylphenyl)propionic acid to **4a** and **5a** by means of an intramolecular Friedel–Crafts acylation was reported to be nonregioselective.[15] The cyclocarbonylation route provides an alternative to the conventional preparation of 2,3-dihydro-1*H*-inden-1-ones.

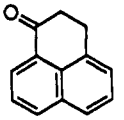
This cyclocarbonylation was successfully applied to a polyaromatic system. The reaction of 1-(1-naphthyl)-2-(trimethylsilyl)acetylene (**11**) gave **12** in excellent yield under the usual reaction conditions (eq 6). The cyclization occurred selectively at the β-position of the naphthalene ring, and the other possible isomer **13** was not obtained.




11

12

Yield 75%



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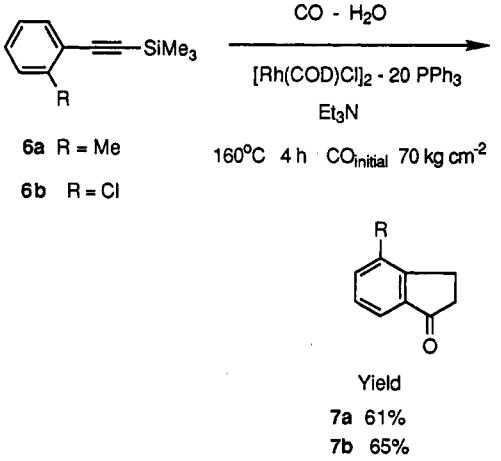
It is well known that 1-aryl-2-(trimethylsilyl)acetylene is easily desilylated by bases.[16] It is possible that phenylacetylene is generated in situ by desilylation of **1a** and

**Table VII. Desilylative Cyclocarbonylation of 3[a]**

| entry | substrate | R | product | yield of 4, %[b] |
|---|---|---|---|---|
| 1 | **3a** | Me | **4a** | 72 |
| 2[c] | **3b** | MeO | **4b** | 52 |
| 3 | **3c** | Ac | **4c** | 79 |
| 4 | **3d** | $CF_3$ | **4d** | 68 |
| 5 | **3e** | $EtO_2C$ | **4e** | 82 |

[a] A mixture of 1 (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), $[Rh(COD)Cl]_2$ (0.05 mmol), $PPh_3$ (2 mmol), and THF (10 mL) was stirred at 160 °C for 4 h under CO ($P_{initial}$ = 70 kg cm$^{-2}$). [b] Isolated yield. [c] **5b** was obtained in 28% yield.

**Scheme II**




6a R = Me

6b R = Cl

Yield

7a 61%

7b 65%

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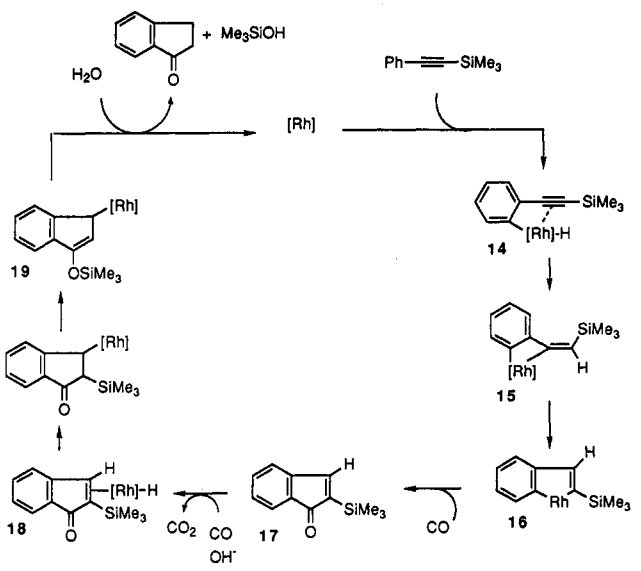
(12) (a) Nakada, Y.; Muramatsu, S.; Asai, M.; Ohno, S.; Yura, Y. *Agric. Biol. Chem.* **1978**, *42*, 1357. (b) Nakada, Y.; Ohno, S.; Yoshimoto, M.; Yura, Y. *Agric. Biol. Chem.* **1978**, *42*, 1365.

(13) Brancaccio, G.; Larizza, A.; Lettieri, G. *J. Med. Chem.* **1981**, *24*, 998.

(14) (a) Zhang, J.; Hertzler, R. L.; Holt, E. M.; Vickstrom, T.; Eisenbraun, E. J. *J. Org. Chem.* **1993**, *58*, 556. (b) Boykin, D. W.; Hertzler, R. L.; Delphin, J. K.; Eisenbraun, E. J. *J. Org. Chem.* **1989**, *54*, 1418. (c) Takeda, K.; Tsuboyama, K.; Takayanagi, H.; Shirokami, R.; Takeura, M.; Ogura, H. *Chem. Pharm. Bull.* **1989**, *37*, 2334. (d) Hulin, B.; Koreeda, M. *J. Org. Chem.* **1984**, *49*, 207. (e) McClure, D. E.; Arison, B. H.; Jones, J. H.; Baldwin, J. J. *J. Org. Chem.* **1981**, *46*, 2431. (f) House, H. O.; McDaniel, W. C. *J. Org. Chem.* **1977**, *42*, 2155. (g) House, H. O.; Budson, C. B. *J. Org. Chem.* **1970**, *35*, 647. (h) Floyd, M. B.; Allen, G. R., Jr. *J. Org. Chem.* **1970**, *35*, 2647. (i) Elsner, B. B.; Parker, K. J. *J. Chem. Soc.* **1957**, 592.

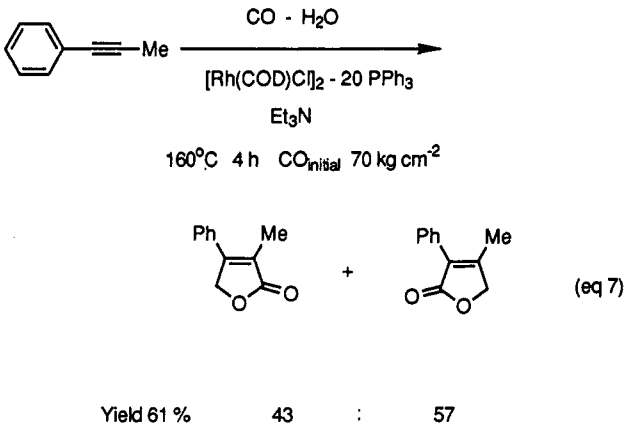
(15) The cyclization of 3-(3-methylphenyl)propionic acid gave a mixture of 5-methyl-2,3-dihydro-1*H*-inden-2-one (**4a**) and 7-methyl-2,3-dihydro-1*H*-inden-2-one (**5a**), see: (a) Budharm, R. S.; Palaniswamy, V. A.; Eisenbraum, E. J. *J. Org. Chem.* **1986**, *51*, 1402. (b) Premasagar, V.; Palaniswamy, V. A.; Eisenbraum, E. J. *J. Org. Chem.* **1981**, *46*, 2974. (c) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590.

**Scheme III**



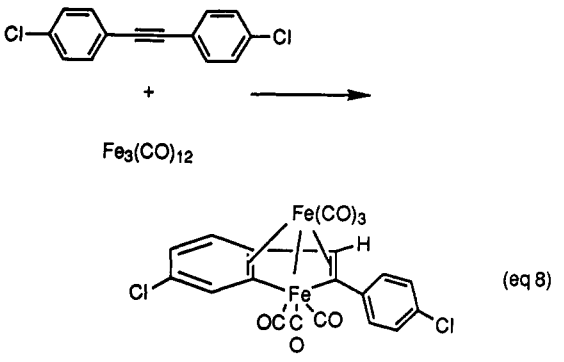

is cyclocarbonylated to give **2a**. This possibility was eliminated by the fact that when we subjected phenylacetylene to the reaction conditions, no cyclization product was obtained.

For comparison with the reaction shown in eq 1, the reaction of 1-phenyl-1-propyne was carried out under the optimized conditions discussed above. A 43:57 mixture of isomeric 2-(5*H*)-furanones was obtained (eq 7). No




2-methyl-3-hydro-1*H*-inden-1-one was obtained. The trimethylsilyl substituent on the acetylenic carbon is necessary for the formation of 2,3-dihydro-1*H*-inden-1-ones.

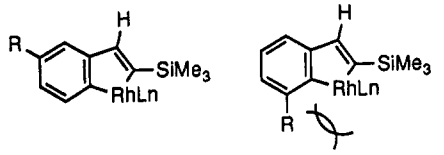
A reaction pathway similar to that for the $Co_2(CO)_8$-catalyzed cyclocarbonylation of diarylacetylenes under water gas shift reaction conditions is also reasonable for our cyclocarbonylation.[6a] A possible reaction mechanism is shown in Scheme III. $\pi$-Complexation of the acetylene to the rhodium induces oxidative addition of the aromatic hydrogen.[17] Intramolecular insertion of the coordinated acetylene into the Rh–H bond results in the formation of complex **15**.[18] Isomerization of **15** affords complex **16**. Ferraindene complex **20**, which is analogous to complex **16**, was obtained from the reaction of bis(4-chlorophenyl)-acetylene with $Fe_3(CO)_{12}$ (eq 8).[19] The insertion of carbon



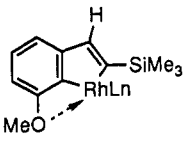

**20**

monoxide into the Rh–C bond gives indenone complex **17**. The hydrogenation of the C–C double bond in **18** by the Rh–H species formed by the water gas shift reaction[20] and subsequent 1,3-rearrangement of the $Me_3Si$ group from carbon to oxygen yield **19**.[21] The hydrolysis of **19** yields **2a** and trimethylsilanol.

Substrates bearing a substituent at the meta position on the aromatic ring cyclized regiospecifically to give a 5-substituted-2,3-dihydro-1*H*-inden-1-one, except for **3b**. The regiospecificity was the result of steric hindrance between the substituent and the rhodium moiety. Intermediate **21** is much more favorable than **22**. In the case of **3b**, product **5b**, which was derived from less-favorable intermediate **22**, was obtained in 35% selectivity.




**21** **22**




**23**

The chelation of the oxygen atom may stabilize intermediate **23**.[22]

(16) (a) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627. (c) The desilylation of 1-*N*-heteroaromatic-2-(trimethylsilyl)acetylene has been reported, see: Sakamoto, T.; Shiraiwa, M.; Kondo, Y.; Yamanaka, H. *Synthesis* **1983**, 312.

(17) Increased electron density on the rhodium facilitates the oxidative addition. Thus, rhodium phosphine species coordinated by a greater number of triphenylphosphines is more catalytically active.

(18) For Rh-catalyzed addition of an aromatic–hydrogen bond to an unsaturated bond, see: (a) Hong, P.; Yamazaki, H.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1978**, 535. (b) Hong, P.; Cho, B.-P.; Yamazaki, H. *Chem. Lett.* **1980**, 507. (c) Sasaki, K.; Sakakura, T.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 685.

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(20) Reductions of $\alpha,\beta$-unsaturated carbonyl compounds under the water gas shift reaction conditions have been reported, see: (a) Kaspar, J.; Spongliarrich, A.; Cernogoraz, A.; Graziani, M. *J. Organomet. Chem.* **1983**, *255*, 371. (b) Alessio, E.; Vinzi, F.; Mestroni, G. *J. Mol. Catal.* **1984**, *22*, 327. (c) Kitamura, T.; Joh, T.; Hagihara, N. *Chem. Lett.* **1975**, 203.

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## Experimental Section

**Materials.** All reagents were dried and purified before use by the usual procedures. Carbon monoxide (>99.9%) was used as received without further purification. $[Rh(COD)Cl]_2$,[23] $RhH(CO)(PPh_3)_3$,[24] $RhCl(PPh_3)_3$,[25] $[Rh(CO)Cl]_2$,[26] $[Rh(COD)_2]BF_4$,[27] and $[Rh(OAc)_2]_2$[28] were prepared by literature methods. $RhCl_3 \cdot xH_2O$ and $Rh_6(CO)_{16}$ were purchased. Silylacetylenes were prepared by a literature method from the corresponding aryl halide and (trimethylsilyl)acetylene.[16b] (Trimethylsilyl)acetylene was purchased.

**General Methods.** Melting points are uncorrected. $^1H$ NMR and $^{13}C$ NMR spectra were recorded in $CDCl_3$ solutions at 270 MHz and 67.8 MHz, respectively, with $Me_4Si$ as an internal standard. IR spectra were obtained from KBr pellets. GC analyses were performed with 3-mm × 2-m glass columns packed with either 20% SE-30 on 60/80 mesh chromosorb w, AW-DMCS or 5% OV-17 on 60/80 mesh chromosorb w, AW-DMCS. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

**General Procedure for the Desilylative Cyclocarbonylation of 1-Aryl-2-(trimethylsilyl)acetylenes.** A mixture of 1-aryl-2-(trimethylsilyl)acetylene (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), THF (10 mL), $[Rh(COD)Cl]_2$ (0.05 mmol), and $PPh_3$ (2.0 mmol) was heated in a 50-mL stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The reactor was sealed and flushed with carbon monoxide, and then it was pressurized with carbon monoxide to 70 kg $cm^{-2}$. The stirred mixture was heated. Reaction temperatures and reaction times are shown in the tables. The reaction was terminated by rapid cooling. The products were isolated by column chromatography.

**Reaction of 1a in the Presence of $D_2O$.** A mixture of 1-phenyl-2-(trimethylsilyl)acetylene (**1a**) (5 mmol), $Et_3N$ (10 mmol), $D_2O$ (50 mmol), THF (10 mL), $[Rh(COD)Cl]_2$ (0.05 mmol), and $PPh_3$ (2.0 mmol) was heated at 160 °C for 4 h in a 50-mL stainless steel autoclave under an initial carbon monoxide pressure of 70 kg $cm^{-2}$. The deuteriated 2,3-dihydro-1*H*-inden-1-one was obtained (0.522 g, 79%) by silica gel chromatography.

**Cyclocarbonylation of Phenylacetylene.** A mixture of phenylacetylene (5 mmol), $Et_3N$ (10 mmol), $H_2O$ (50 mmol), THF (10 mL), $[Rh(COD)Cl]_2$ (0.05 mmol), and $PPh_3$ (2.0 mmol) was heated at 160 °C for 4 h in a 50-mL stainless steel autoclave under an initial carbon monoxide pressure of 70 kg $cm^{-2}$. The reaction was terminated by rapid cooling. The resulting mixture was analyzed by gas chromatography.

**2,3-Dihydro-1*H*-inden-1-one (2a)**: mp 39–41 °C (lit.[29] mp 42 °C); $^1H$ NMR δ 2.64–2.69 (m, 2H, $CH_2$), 3.13 (t, 2H, $J$ = 5.61 Hz, $CH_2$), 7.35 (t, 1H, $J$ = 7.59 Hz, arom), 7.47 (d, 1H, $J$ = 7.59 Hz, arom), 7.57 (t, 1H, $J$ = 7.59 Hz, arom), 7.74 (d, 1H, $J$ = 7.59 Hz, arom); $^{13}C$ NMR δ 25.6 ($CH_2$), 36.1 ($CH_2$), 123.5 (arom), 126.6 (arom), 127.1 (arom), 134.4 (arom), 136.9 (arom), 155.0 (arom), 206.8 (C=O); IR 1700 $cm^{-1}$.

**6-Methyl-2,3-dihydro-1*H*-inden-1-one (2b)**: mp 63 °C (lit.[30] mp 62–63 °C); $^1H$ NMR δ 2.39 (s, 3H, $CH_3$), 2.63–2.68 (m, 2H, $CH_2$), 3.07 (t, 2H, $J$ = 5.94 Hz, $CH_2$), 7.32–7.40 (m, 2H, arom), 7.53 (s, 1H, arom); $^{13}C$ NMR δ 20.9 ($CH_3$), 25.3 ($CH_2$), 36.4 ($CH_2$), 123.4 (arom), 126.2 (arom), 135.7 (arom), 137.0 (arom), 137.1 (arom), 152.4 (arom), 207.0 (C=O); IR 1705 $cm^{-1}$. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90; O, 10.94. Found: C, 82.13; H, 6.87.

**6-Methoxy-2,3-dihydro-1*H*-inden-1-one (2c)**: mp 103–106 °C (lit.[14c] mp 107–109 °C); $^1H$ NMR δ 2.68–2.72 (m, 2H, $CH_2$), 3.06 (t, 2H, $J$ = 5.94 Hz, $CH_2$), 3.82 (s, 3H, $OCH_3$), 7.15–7.20 (m, 2H, arom), 7.34–7.37 (m, 1H, arom); $^{13}C$ NMR δ 25.0 ($CH_2$), 36.9 ($CH_2$), 55.4 ($OCH_3$), 104.8 (arom), 123.9 (arom), 127.2 (arom), 138.1 (arom), 147.8 (arom), 159.3 (arom), 206.8 (C=O); IR 1690 $cm^{-1}$. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21; O, 19.73. Found: C, 73.89; H, 6.19.

**6-Chloro-2,3-dihydro-1*H*-inden-1-one (2d)**: mp 77–80 °C (lit.[31] mp 81 °C); $^1H$ NMR δ 2.69–2.74 (m, 2H, $CH_2$), 3.11 (t, 2H, $J$ = 5.94 Hz, $CH_2$), 7.41 (d, 1H, $J$ = 8.25 Hz, arom), 7.53 (dd, 1H, $J$ = 8.25, 1.98 Hz, arom), 7.68 (d, 1H, $J$ = 1.98 Hz, arom); $^{13}C$ NMR δ 25.4 ($CH_2$), 36.6 ($CH_2$), 123.4 (arom), 127.8 (arom), 133.6 (arom), 134.5 (arom), 138.5 (arom), 153.1 (arom), 205.4 (C=O); IR 1705 $cm^{-1}$. Anal. Calcd for $C_9H_7OCl$: C, 64.88; H, 4.24; O, 9.60; Cl 21.26. Found: C, 64.82; H, 4.19, Cl 21.17.

**6-(Ethoxycarbonyl)-2,3-dihydro-1*H*-inden-1-one (2e)**: mp 76–77 °C; $^1H$ NMR δ 1.41 (t, 3H, $J$ = 7.26 Hz, $OCH_2CH_3$), 2.72–2.77 (m, 2H, $CH_2$), 3.21 (t, 2H, $J$ = 6.27 Hz, $CH_2$), 4.39 (q, 2H, $J$ = 7.26 Hz, $OCH_2CH_3$), 7.55 (d, 1H, $J$ = 7.92 Hz, arom), 8.26 (dd, 1H, $J$ = 7.92, 1.65 Hz, arom), 8.39 (s, 1H, arom); $^{13}C$ NMR δ 14.1 ($CH_3$), 25.9 ($CH_2$), 36.3 ($CH_2$), 61.2 ($OCH_2CH_3$), 125.0 (arom), 126.7 (arom), 130.0 (arom), 135.2 (arom), 137.1 (arom), 159.3 (arom), 165.6 (C=O), 205.8 (C=O); IR 1700 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; O, 23.50. Found: C, 70.42; H, 5.91.

**6-Acetyl-2,3-dihydro-1*H*-inden-1-one (2f)**: mp 97–100 °C (lit.[32] mp 98 °C); $^1H$ NMR δ 2.64 (s, 3H, $CH_3$), 2.74–2.79 (m, 2H, $CH_2$), 3.22 (t, 2H, $J$ = 5.94 Hz, $CH_2$), 7.59 (d, 1H, $J$ = 8.25 Hz, arom), 8.22 (dd, 1H, $J$ = 7.92, 1.65 Hz, arom), 8.26 (s, 1H, arom); $^{13}C$ NMR δ 25.9 ($CH_2$), 26.5 ($CH_3$), 36.3 ($CH_2$), 123.8 (arom), 127.0 (arom), 133.6 (arom), 136.4 (arom), 137.2 (arom), 160.0 (arom), 196.9 (C=O), 206.8 (C=O); IR 1705 $cm^{-1}$. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; O, 18.37. Found: C, 75.57; H, 5.76.

**6-Cyano-2,3-dihydro-1*H*-inden-1-one (2g)**: mp 108 °C $^1H$ NMR δ 2.75–2.80 (m, 2H, $CH_2$), 3.27 (t, 2H, $J$ = 5.93 Hz, $CH_2$), 7.66 (d, 1H, $J$ = 7.92 Hz, arom), 7.84 (d, 1H, $J$ = 7.91 Hz, arom), 7.99 (s, 1H, arom); $^{13}C$ NMR δ 26.1 ($CH_2$), 35.9 ($CH_3$), 111.4 (arom), 117.9 (CN), 127.7 (arom), 127.9 (arom), 136.9 (arom), 137.5 (arom), 159.0 (arom), 204.5 (C=O); IR 2230, 1710 $cm^{-1}$. Anal. Calcd for $C_{10}H_7NO$: C, 76.42; H, 4.49; N, 8.91, O, 10.18. Found: C, 76.69; H, 4.35; N, 8.95.

**5-Methyl-2,3-dihydro-1*H*-inden-1-one (4a)**: mp 67–71 °C (lit.[15a] mp 71–73 °C); $^1H$ NMR δ 2.43 (s, 3H, $CH_3$), 2.63–2.68 (m, 2H, $CH_2$), 3.07 (t, 2H, $J$ = 5.61 Hz, $CH_2$), 7.17 (d, 1H, $J$ = 7.59 Hz, arom), 7.26 (d, 1H, $J$ = 0.66 Hz, arom), 7.64 (d, 1H, $J$ = 7.92 Hz, arom); $^{13}C$ NMR δ 21.9 ($CH_3$), 25.6 ($CH_2$), 36.3 ($CH_2$), 123.4 (arom), 126.9 (arom), 128.5 (arom), 134.8 (arom), 145.7 (arom), 155.6 (arom), 206.5 (C=O); IR 1690 $cm^{-1}$. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90; O, 10.94. Found: C, 82.01; H, 6.98.

**5-Methoxy-2,3-dihydro-1*H*-inden-1-one (4b)**: mp 112 °C (lit.[33] mp 111 °C); $^1H$ NMR δ 2.63–2.67 (m, 2H, $CH_2$), 3.07 (t, 2H, $J$ = 6.27 Hz, $CH_2$), 3.87 (s, 3H $OCH_3$), 6.87–6.90 (m, 2H, arom), 7.65–7.69 (s, 1H, arom); $^{13}C$ NMR δ 25.7 ($CH_2$), 36.3 ($CH_2$), 55.5 ($OCH_3$), 109.6 (arom), 115.2 (arom), 125.1 (arom), 130.3 (arom), 158.1 (arom), 165.1 (arom), 205.1 (C=O); IR 1690 $cm^{-1}$. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21; O, 19.73. Found: C, 73.79; H, 6.40.

**7-Methoxy-2,3-dihydro-1*H*-inden-1-one (5b)**: mp 102–103 °C (lit.[34] mp 102–103 °C); $^1H$ NMR δ 2.63–2.67 (m, 2H, $CH_2$), 3.07 (t, 2H, $J$ = 6.27 Hz, $CH_2$), 3.94 (s, 3H $OCH_3$), 6.78 (d, 1H, $J$ = 7.59 Hz, arom), 7.00 (dd, 1H, $J$ = 7.59, 0.66 Hz, arom), 7.51 (t, 1H, $J$ = 7.59 Hz, arom); $^{13}C$ NMR δ 25.3 ($CH_2$), 36.6 ($CH_2$), 55.5 ($OCH_3$), 108.6 (arom), 118.2 (arom), 124.9 (arom), 136.2 (arom), 157.8 (arom), 157.9 (arom), 204.6 (C=O); IR 1700 $cm^{-1}$. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21; O, 19.73. Found: C, 73.77; H, 6.26.

**5-Acetyl-2,3-dihydro-1*H*-inden-1-one (4c)**: mp 89 °C; $^1H$ NMR δ 2.66 (s, 3H, $CH_3$), 2.73–2.78 (m, 2H, $CH_2$), 3.22 (t, 2H, $J$ = 5.61 Hz, $CH_2$), 7.80 (d, 1H, $J$ = 7.92 Hz, arom), 7.93 (d, 1H, $J$ = 7.92 Hz, arom), 8.05 (s, 1H, arom); $^{13}C$ NMR δ 25.7 ($CH_2$), 27.0 ($CH_3$), 36.4 ($CH_2$), 123.7 (arom), 126.4 (arom), 127.2 (arom), 140.0 (arom), 141.6 (arom), 155.0 (arom), 197.6 (C=O), 206.1

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(C=O); IR 1700, 1680 cm$^{-1}$. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; O, 18.37. Found: C, 75.74; H, 5.87.

**5-(Trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one (4d)**: mp 59–60 °C; $^1$H NMR $\delta$ 2.75–2.79 (m, 2H, C$H_2$), 3.23 (t, 2H, $J$ = 6.27 Hz, C$H_2$), 7.63 (d, 1H, $J$ = 7.92 Hz, arom), 7.77 (s, 1H, arom), 7.85 (d, 1H, $J$ = 7.92 Hz, arom); $^{13}$C NMR $\delta$ 25.7 (*C*H$_2$), 36.2 (*C*H$_2$), 123.6 (q, *C*F$_3$, $J_{C-F}$ = 273.4 Hz), 123.8 (q, $J_{C-F}$ = 3.6 Hz, arom), 124.1 (arom), 124.3 (q, $J_{C-F}$ = 3.6 Hz, arom), 129.6 (arom), 135.7 (q, $J_{C-F}$ = 31.8 Hz, arom), 139.6 (arom), 205.5 (C=O); IR 1710 cm$^{-1}$. Anal. Calcd for $C_{10}H_7F_3O$: C, 60.00; H, 3.52; F, 28.47; O, 7.99. Found: C, 60.15; H, 3.37; F, 28.23.

**5-(Ethoxycarbonyl)-2,3-dihydro-1*H*-inden-1-one (4e)**: mp 63 °C; $^1$H NMR $\delta$ 1.43 (t, 3H, $J$ = 7.26 Hz, OCH$_2$C*H*$_3$), 2.73–2.77 (m, 2H, C*H*$_2$), 3.20 (t, 2H, $J$ = 5.94 Hz, C*H*$_2$), 4.42 (q, 2H, $J$ = 7.26 Hz, OC*H*$_2$CH$_3$), 7.78 (d, 1H, $J$ = 7.92 Hz, arom), 8.03 (d, 1H, $J$ = 7.92 Hz, arom), 8.15 (s, 1H, arom); $^{13}$C NMR $\delta$ 14.1 (*C*H$_3$), 25.6 (*C*H$_2$), 36.4 (*C*H$_2$), 61.4 (O*C*H$_2$CH$_3$), 123.4 (arom), 127.9 (arom), 128.4 (arom), 135.7 (arom), 140.0 (arom), 154.7 (arom), 165.7 (C=O), 206.2 (C=O); IR 1715, 1700 cm$^{-1}$. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; O, 23.50. Found: C, 70.58; H, 5.94.

**4-Methyl-2,3-dihydro-1*H*-inden-1-one (7a)**: mp 100 °C (lit.[35] mp 101–104 °C); $^1$H NMR $\delta$ 2.35 (s, 3H, C*H*$_3$), 2.65–2.69 (m, 2H, C*H*$_2$), 3.00 (t, 2H, $J$ = 5.28 Hz, C*H*$_2$), 7.27 (t, 1H, $J$ = 7.26 Hz, arom), 7.39 (d, 1H, $J$ = 7.26 Hz, arom), 7.58 (d, 1H, $J$ = 7.59 Hz, arom); $^{13}$C NMR $\delta$ 17.6 (*C*H$_3$), 24.5 (*C*H$_2$), 36.0 (*C*H$_2$), 120.9 (arom), 127.3 (arom), 134.9 (arom), 135.8 (arom), 136.7 (arom), 154.0 (arom), 207.2 (C=O); IR 1700 cm$^{-1}$. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90; O, 10.94. Found: C, 81.78; H, 6.78.

**4-Chloro-2,3-dihydro-1*H*-inden-1-one (7b)**: mp 93–94 °C (lit.[36] mp 93–95 °C); $^1$H NMR $\delta$ 2.70–2.74 (m, 2H, C*H*$_2$), 3.11 (t, 2H, $J$ = 6.27 Hz, C*H*$_2$), 7.33 (t, 1H, $J$ = 7.59 Hz, arom), 7.57 (dd, 1H, $J$ = 7.59, 0.99 Hz, arom), 7.64 (d, 1H, $J$ = 7.59 Hz, arom); $^{13}$C NMR $\delta$ 24.8 (*C*H$_2$), 35.9 (*C*H$_2$), 121.9 (arom), 128.8 (arom), 132.8 (arom), 134.1 (arom), 138.9 (arom), 152.5 (arom), 205.7 (C=O); IR 1700 cm$^{-1}$. Anal. Calcd for $C_9H_7OCl$: C, 64.88; H, 4.24; O, 9.60; Cl 21.26. Found: C, 64.80; H, 4.40, Cl 21.28.

**2,3,6,7-Tetrahydro-*s*-indacene-1,5-dione (9)**: mp 239 °C (lit.[37] mp 230–231 °C); $^1$H NMR $\delta$ 2.77–2.82 (m, 4H, C*H*$_2$), 3.21 (t, 4H, $J$ = 5.94 Hz, C*H*$_2$), 7.82 (s, 2H, arom); $^{13}$C NMR $\delta$ 25.5 (*C*H$_2$), 37.0 (*C*H$_2$), 121.6 (arom), 141.8 (arom), 153.4 (arom), 206.5 (C=O); IR 1710 cm$^{-1}$. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41; O, 17.18. Found: C, 77.35; H, 5.41.

**1,2-Dihydrocyclopenta[*a*]naphthalen-1-one (12)**: mp 121–122 °C (lit.[38] mp 120 °C); $^1$H NMR $\delta$ 2.76–2.80 (m, 2H, C*H*$_2$), 3.34 (t, 2H, $J$ = 5.61 Hz, C*H*$_2$), 7.56–7.77 (m, 4H, arom), 7.88–7.92 (m, 1H, arom), 7.97–8.00 (m, 1H, arom); $^{13}$C NMR $\delta$ 24.2 (*C*H$_2$), 36.0 (*C*H$_2$), 119.3 (arom), 124.3 (arom), 126.9 (arom), 128.3 (arom), 128.8 (arom), 129.1 (arom), 130.4 (arom), 134.5 (arom), 136.4 (arom), 156.2 (arom), 206.6 (C=O); IR 1700 cm$^{-1}$. Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53; O, 8.78. Found: C, 85.41; H, 5.51.

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**Reaction of 1a under Carbon Monoxide and Hydrogen Pressure.** A mixture of 1-phenyl-2-(trimethylsilyl)acetylene (1a) (5 mmol), Et$_3$N (10 mmol), THF (10 mL), [Rh(COD)Cl]$_2$ (0.05 mmol), and PPh$_3$ (2.0 mmol) was heated in a 50-mL stainless steel autoclave. The reactor was sealed and was flushed with carbon monoxide. The reactor was pressurized with carbon monoxide to 50 kg cm$^{-2}$, and then it was pressurized with hydrogen to 100 kg cm$^{-2}$. The reaction was carried out at 160 °C for 4 h. The reaction was terminated by rapid cooling. The solvent was evaporated in vacuo. Silica gel chromatography of the residue gave two fractions. The early fraction (20:1 hexane–EtOAc) gave 0.577 g of a mixture of 2-phenyl-3-(trimethylsilyl)propanal and 3-phenylpropanal. The ratio of these aldehydes was determined by $^1$H NMR. The later fraction (9:1 hexane–EtOAc) gave 0.070 g of 2,3-dihydro-1*H*-inden-1-one. 3-Phenylpropanal was identified by comparison of its spectrum with that of an authentic sample.

**2-Phenyl-3-(trimethylsilyl)propanal.** $^1$H NMR $\delta$ −1.36 (s, 9H, Si(C*H*$_3$)$_3$), 1.03 (dd, 1H, $J$ = 14.52, 9.57 Hz, C*H*$_2$SiMe$_3$), 1.28 (dd, 1H, $J$ = 14.52, 5.61 Hz, C*H*$_2$SiMe$_3$), 3.54 (ddd, 1H, $J$ = 9.57, 5.61, 2.31 Hz, PhC*H*CHO), 7.14–7.39 (m, 5H, Ph), 9.58 (d, $J$ = 2.31 Hz, C*H*O); $^{13}$C NMR $\delta$ −1.4 (Si(*C*H$_3$)$_3$), 16.8 (*C*H$_2$Si(CH$_3$)$_3$), 54.9 (Ph*C*H), 127.4 (arom), 128.6 (arom), 128.8 (arom), 137.7 (arom), 200.7 (C=O); IR 1720 cm$^{-1}$.

**Reaction of 1-Phenyl-1-propyne.** A mixture of 1-phenyl-1-propyne (5 mmol), Et$_3$N (10 mmol), H$_2$O (50 mmol), THF (10 mL), [Rh(COD)Cl]$_2$ (0.05 mmol), and PPh$_3$ (2.0 mmol) was heated at 160 °C for 4 h in a 50-mL stainless steel autoclave under an initial carbon monoxide pressure of 70 kg cm$^{-2}$. The reaction was terminated by rapid cooling. The solvent was evaporated in vacuo. The products were separated by silica gel chromatography, which gave two fractions. The early fraction (4:1 hexane–EtOAc) gave 0.261 g of 2-methyl-3-phenylfuran-2(5*H*)-one. The later fraction (4:1 hexane–EtOAc) gave 0.341 g of 2-phenyl-3-methylfuran-2(5*H*)-one. Furanones were identified by comparison of their spectra with those in the literature.[39]

**2-Methyl-3-phenylfuran-2(5*H*)-one**: $^1$H NMR $\delta$ 2.13 (s, 3H, C*H*$_3$), 5.05 (s, 2H, C*H*$_2$O), 7.42–7.49 (m, 5H, phenyl); $^{13}$C NMR $\delta$ 10.2 (*C*H$_3$), 70.4 (*C*H$_2$O), 122.8 (vinyl), 127.1 (phenyl), 129.0 (phenyl), 130.1 (phenyl), 131.3 (vinyl), 154.8 (phenyl), 175.4 (C=O); IR 1740 cm$^{-1}$.

**2-Phenyl-3-methylfuran-2(5*H*)-one**: $^1$H NMR $\delta$ 2.19 (s, 3H, C*H*$_3$), 4.76 (s, 2H, C*H*$_2$O), 7.32–7.50 (m, 5H, phenyl); $^{13}$C NMR $\delta$ 13.2 (*C*H$_3$), 72.3 (*C*H$_2$O), 126.5 (vinyl), 128.3 (phenyl), 128.4 (phenyl), 128.7 (phenyl), 129.8 (vinyl), 157.8 (phenyl), 173.2 (C=O); IR 1750 cm$^{-1}$.

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