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Rhodium-catalyzed carbonylation of alkynes having a carbonyl group adjacent to carbon–carbon triple bond under water–gas shift reaction conditions

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Abstract

Under water–gas shift reaction conditions, the carbonylation reaction of 2-phenylethynylbenzaldehyde catalyzed by $Rh_6(CO)_{16}$ gave a tricyclic lactone, indeno[2,1-*b*]furan, while the reaction of 2-phenylethynylbenzoate resulted in the formation of a tetracyclic lactone, indeno[1,2-*c*]isocoumarin. The tri- and tetra-cyclic lactones are cyclic carbonylation products of the alkynes which arose from participation of the carbonyl group in formyl and alkoxycarbonyl substituents adjacent to the carbon–carbon triple bond in the cyclic carbonylation. The carbonylation reactions are strongly affected by the reaction temperature, and seem to proceed via a different pathway depending on the temperature.

Keywords: Rhodium catalyst; Cyclic carbonylation; Tricyclic lactone; Tetracyclic lactone

1. Introduction

Carbonylation reactions have long continued to attract much interest and have been widely applied to organic syntheses (see for example, Ref. [1]). The carbonylation of unsaturated substrates such as alkenes and alkynes under water–gas shift reaction (WGSR) conditions often gives novel products by the catalysis of transition metal carbonyls such as $Fe(CO)_5$ [2–4], $Ru_3(CO)_{12}$ [5,6], $Rh_6(CO)_{16}$ [7–9], and some reviews on the WGS reactions have also been published [10]. Of special interest is cyclic carbonylation giving heterocyclic products, which may be employed as important intermediates leading to bioactive substances. Such examples include the preparation of furanones by cyclic carbonylation of alkynes [11–13]. We have previously reported the rhodium-catalyzed carbonylation of alkynes giving furan-2(5*H*)-ones under water–gas shift reaction conditions [14]. In such a reaction, furanone was formed by the incorporation of one molecule of acetylene, two molecules of carbon

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monoxide, and one molecule of hydrogen which originates from water. It is noteworthy that the carbonylation is characteristic to the WGSR conditions and the similar reaction under syn gas ($CO + H_2$) conditions yields hydroxy methylation products from alkynes. Recently, our interest has been focused on the carbonylation of alkynes bearing functional groups such as amino [15] and hydroxyl groups [16] adjacent to the carbon–carbon triple bond under the WGSR conditions. These reactions gave heterocyclic products, which arose from the participation of the functional groups in the cyclization. We have now found new types of cyclic carbonylation in which the formyl functional group in 2-phenylethynylbenzaldehyde as well as the alkoxycarbonyl group in 2-phenylethynylbenzoate incorporate in the reaction to afford novel fused heterocyclic products, indeno[2,1-*b*]furan and indeno[1,2-*c*]isocoumarin, respectively. The preliminary result has been communicated [17,18], and we report here the full detail of these two new reactions.

2. Experimental

Melting points were recorded on a Yamato Melting Point Apparatus Model MP-21 and are uncorrected. IR spectra were obtained with a Perkin-Elmer 2000 infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-EX270 or JNM-LA400 FT NMR system in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were obtained using a Shimadzu GCMS-QP2000 spectrometer. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Analytical HPLC was performed on a Nakarai 5SL (4.6 × 250 mm) chromatography.

2.1. Materials

Solvents and reagents were dried and purified prior to use according to standard procedures. $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ and $[Rh(CO)_2Cl]_2$ were prepared by the methods described in Refs. [19–21]. All other chemicals are commercially available reagents and were used without purification. The 2-substituted phenylacetylenes were prepared by the palladium-catalyzed cross-coupling between 2-substituted bromobenzenes and terminal acetylenes by the procedure developed in our laboratory [22].

2.2. General preparation of ethynyl compounds ***1a–y***

To a mixture of acetylenic compound (30 mmol) and 2-bromobenzaldehyde (or 2-iodobenzoate) (20 mmol) in triethylamine (200 ml) were added $PdCl_2(PPh_3)_2$ (0.2 mmol), PPh_3 (0.75 mmol), and CuI (1.15 mmol). The mixture was stirred at 80°C for 8 h under nitrogen and then the solvent was removed under reduced pressure. The resulting residue was passed through a silica gel column with hexane–benzene (6:1) as an eluent to give the ethynyl compounds.

2.3. Phenylethynylbenzaldehyde ***1a***

Pale yellow oil (3.22 g, 79% yield); IR (neat) 1698 cm^{-1} (ν_{CO}), 2216 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.3 (s, 1H, –CHO), 7.20–6.30 (m, 9H, aromatic ring); MS m/z 206 (M^+).

2.4. (4-Methoxyphenyl)ethynylbenzaldehyde **1b**

Pale yellow powders (1.90 g, 40%); IR (neat) 1697 cm^{-1} (ν_{CO}), 2213 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.7 (s, 1H, –CHO), 8.00–6.83 (m, 8H, aromatic ring), 3.85 (s, 3H, OCH_3); MS m/z 236 (M^+).

2.5. (4-Carbonylethoxyphenyl)ethynylbenzaldehyde **1c**

Pale yellow powders (1.90 g, 40%); IR (neat) 1697, 1705 cm^{-1} (ν_{CO}), 2213 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.5 (d, 1H, –C*H*O), 8.02–7.33 (m, 8H, aromatic ring), 4.30 (q, 2H, $J = 6.8$ Hz, $CO_2CH_2CH_3$), 1.33 (t, 3H, $J = 6.9$ Hz, $CO_2CH_2CH_3$); MS m/z 278 (M^+).

2.6. (Prop-1-ynyl)benzaldehyde **1d**

Pale yellow crystals (recrystallization by ethanol, 2.02 g, 70%); IR (neat) 1697 cm^{-1} (ν_{CO}), 2211 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.5 (s, 1H, –C*H*O), 7.90–7.30 (m, 4H, aromatic ring), 1.50 (s, 3H, CC*H*$_3$); MS m/z 144 (M^+).

2.7. (Hex-1-ynyl)benzaldehyde **1e**

Pale yellow oil (2.62 g, 71%); IR (neat) 1697 cm^{-1} (ν_{CO}), 2228 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.5 (d, 1H, –C*H*O), 7.90–7.30 (m, 4H, aromatic ring), 2.49–0.96 (m, 9H, C*H*$_2$C*H*$_2$-C*H*$_2$C*H*$_3$); MS m/z 186 (M^+).

2.8. Ethynylbenzaldehyde **1f**

Treatment of 2-trimethylsilylethynylbenzaldehyde (5.40 g, 26.7 mmol) with methanol, H_2O and K_2CO_3 gave *title compound* **1f** as pale yellow powder (3.30 g, 95%); IR (neat) 1690 cm^{-1} (ν_{CO}), 2109 cm^{-1} (ν_{CC}), 2910, 2810 cm^{-1} (ν_{CHO}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.5 (s, 1H, –C*H*O), 7.95–7.49 (m, 4H, aromatic ring), 3.47 (s, 1H, CC*H*); MS m/z 130 (M^+).

2.9. Phenylethnylbenzacetophenone **1g**

Pale yellow oil (1.45 g, 66%); IR (neat) 1687 cm^{-1} (ν_{CO}), 2215 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.76–7.33 (m, 9H, aromatic ring), 2.78 (s, 3H, COC*H*$_3$); MS m/z 220 (M^+).

2.10. Phenylethynylbenzbenzophenone **1h**

Pale yellow oil (4.39 g, 71%); IR (neat) 1675 cm^{-1} (ν_{CO}), 2215 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 8.01–7.39 (m, 14H, aromatic ring); MS m/z 282 (M^+).

2.11. Phenylethynylbenzyldehyde **1j**

According to the preparative procedure, the reaction of phenylacetylene with 2-(2-bromophenyl)ethanol, prepared from 2-bromophenylacetic acid, gave 2-(2-phenylethynyl)phenylethanol (94% yield), which was converted to *title compound* **1j** as pale yellow oil (1.20 g, 60%); IR (neat) 1720 cm^{-1} (ν_{CO}), 2215 cm^{-1} (ν_{CC}), 2830, 2725 cm^{-1} (ν_{CHO}); ^1H NMR (270 MHz, $CDCl_3$) δ 9.80 (t, 1H, $J = 2.0$ Hz, $-CH_2CHO$), 7.62–7.23 (m, 9H, aromatic ring), 3.92 (d, 2H, $J = 2.0$ Hz, $-CH_2CHO$); MS m/z 220 (M^+).

2.12. Phenyl-4-pentynal **1k**

According to the preparative procedure, the reaction of bromobenzene and 4-pentynal gave 5-phenyl-4-pentynal (85% yield), which was converted to *title compound* **1k** as colorless oil (75% yield); IR (neat) 1720 cm^{-1} (ν_{CO}), 2215 cm^{-1} (ν_{CC}), 2830, 2725 cm^{-1} (ν_{CHO}); ^1H NMR (270 MHz, $CDCl_3$) δ 9.80 (s, 1H, $-CHO$), 7.40–7.30 (m, 5H, aromatic ring), 2.83–2.66 (m, 4H, $-CH_2CH_2$-CHO); MS m/z 158 (M^+).

2.13. (2-Formylphenyl)ethynylbenzaldehyde **1m**

Crystal needles (50% yield); IR (KBr) 1698 cm^{-1} (ν_{CO}), 2210 cm^{-1} (ν_{CC}), 2832, 2746 cm^{-1} (ν_{CHO}); ^1H NMR (270 MHz, $CDCl_3$) δ 10.6 (s, 2H, $-CHO$), 8.00–7.51 (m, 8H, aromatic ring); MS m/z 234 (M^+).

2.14. Preparation of ethyl 2-phenylethynylbenzoate **1p**

Yellow oil (76% yield), 160°C (0.10 mm Hg); IR (neat) 1727 cm^{-1} (ν_{CO}), 2218 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.98–7.25 (m, 9H, aromatic ring), 4.42 (q, 2H, $J = 7.5$ Hz, $CO_2CH_2CH_3$), 1.39 (t, 3H, $J = 7.5$ Hz, $CO_2CH_2CH_3$); MS m/z 250 (M^+).

2.15. Ethyl 2-(4-methylphenyl)ethynylbenzoate **1q**

Pale yellow oil (87% yield), 190°C (0.15 mm Hg); IR (neat) 1727 cm^{-1} (ν_{CO}), 2217 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.97–7.15 (m, 8H, aromatic ring), 4.41 (q, 2H, $J = 7.3$ Hz, $CO_2CH_2CH_3$), 2.36 (s, 3H, $ArCH_3$), 1.40 (t, 3H, $J = 7.3$ Hz, $CO_2CH_2CH_3$); MS m/z 264 (M^+).

2.16. Ethyl 2-(4-acetylphenyl)ethynylbenzoate **1r**

Pale yellow oil (62% yield), 190°C (0.10 mm Hg); IR (neat) 1725 cm^{-1} (ν_{CO}), 2218 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.96–7.30 (m, 8H, aromatic ring), 4.42 (q, 2H, $J = 7.0$ Hz, $CO_2CH_2CH_3$), 2.61 (s, 3H, $ArCOCH_3$), 1.40 (t, 3H, $J = 7.3$ Hz, $CO_2CH_2CH_3$); MS m/z 292 (M^+).

2.17. Ethyl 2-(4-methoxyphenyl)ethynylbenzoate **1s**

Pale yellow oil (85% yield), 200°C (0.15 mm Hg); IR (neat) 1724 cm^{-1} (ν_{CO}), 2218 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.79–6.69 (m, 8H, aromatic ring), 4.24 (q, 2H, $J = 7.2$ Hz, $CO_2CH_2CH_3$), 3.61 (s, 3H, $ArOCH_3$), 1.22 (t, 3H, $J = 7.0$ Hz, $CO_2CH_2CH_3$); MS m/z 280 (M^+).

2.18. Di(2-ethoxycarbonylphenyl)acetylene **1u**

According to the preparative procedure, the reaction of ethyl 2-iodobenzoate with ethyl *o*-ethynylbenzoate to give *title compound* **1u** as pale yellow crystals (71% yield); IR (KBr) 1720 cm^{-1} (ν_{CO}), 2215 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 8.00–7.36 (m, 8H, aromatic ring), 4.24 (q, 4H, $J = 7.0$ Hz, $CO_2CH_2CH_3$), 1.22 (t, 6H, $J = 7.0$ Hz, $CO_2CH_2CH_3$); MS m/z 322 (M^+).

2.19. Methyl 2-phenylethynylbenzoate **1v**

Yellow oil (69% yield), 140°C (0.10 mm Hg); IR (neat) 1731 cm^{-1} (ν_{CO}), 2218 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.97–7.32 (m, 9H, aromatic ring), 3.94 (s, 3H, CO_2CH_3); MS m/z 236 (M^+).

2.20. Isopropyl 2-phenylethynylbenzoate **1w**

Yellow oil (81% yield), 175°C (0.10 mm Hg); IR (neat) 1722 cm^{-1} (ν_{CO}), 2217 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 7.97–7.33 (m, 9H, aromatic ring), 5.30 (q, 1H, $J = 6.1$ Hz, $CO_2CH(CH_3)_2$), 1.38 (d, 6H, $J = 6.3$ Hz, $CO_2CH(CH_3)_2$); MS m/z 264 (M^+).

2.21. Phenyl 2-phenylethynylbenzoate **1x**

Colorless crystals (74% yield); IR (neat) 1720 cm^{-1} (ν_{CO}), 2224 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 8.17–7.25 (m, 14H, aromatic ring); MS m/z 298 (M^+).

2.22. Ethyl 4-phenylethynylbenzoate **1y**

Pale yellow oil (60% yield), 160°C (0.10 mm Hg); IR (neat) 1715 cm^{-1} (ν_{CO}), 2222 cm^{-1} (ν_{CC}); ^1H NMR (270 MHz, $CDCl_3$) δ 8.04–7.30 (m, 9H, aromatic ring), 4.39 (q, 2H, $J = 7.0$ Hz, $CO_2CH_2CH_3$), 1.42 (t, 3H, $J = 7.2$ Hz, $CO_2CH_2CH_3$); MS m/z 250 (M^+).

2.23. General procedure for carbonylation of ethynyl compounds

Method A (carbonylation of compounds **1a–p**): a mixture of compound **1** (3 mmol), $Rh_6(CO)_{16}$ (0.01 mmol), NEt_3 (3 mmol), and H_2O (12 mmol) in chloroform (45 ml) was placed in a 100 ml stainless steel autoclave and stirred under 100 atm of carbon monoxide at 80°C. After removal of the solvent from the reaction mixture under reduced pressure, TLC analysis of the residue showed

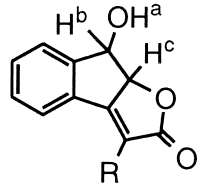
formation of three kinds of products, which were separated by column chromatography on silica gel with an eluent of CH_2Cl_2–Et_2O (20:1). Isolation and recrystallization from ethanol gave product **2**, and furanones **3** and **4**.

Method B (carbonylation of compounds **1p–y**): a mixture of compound **1** (4 mmol), $Rh_6(CO)_{16}$ (0.012 mmol), PPh_3 (0.24 mmol), NEt_3 (1.6 ml), and H_2O (0.4 ml) in dioxane (40 ml) was placed in a 100 ml stainless steel autoclave and stirred under 100 atm of carbon monoxide at 180°C for 15–60 h. After removal of the solvent from the reaction mixture under reduced pressure, TLC analysis of the residue showed formation of two kinds of products, which were separated by column chromatography on silica gel with an eluent of hexane–ethylacetate (3:1). Isolation and recrystallization from hexane–ether gave products **5** and **6**.

*2.24. Carbonylation of compound **1a***

According to method A, the carbonylation of **1a** was carried out for 5 h to give products **2a** and **4a**, but **3a** could not be isolated although it can be detected by the ^{1}H NMR spectrum.

2a: Colorless crystals, 59% HPLC yield (42% isolated yield); mp 191.5–192.3°C; IR (KBr) 3503 cm^{-1} (ν_{OH}), 1755 cm^{-1} (ν_{CO}); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.83–7.13 (m, 9H, Ph), 5.40 (d, 1H, $J = 5.3$, H^c), 5.10 (dd, 1H, $J = 5.0$, 5.3 Hz, H^b), 3.08 (d, 1H, $J = 5.0$ Hz, H^a); MS m/z 264 (M^+). Anal. calc. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.16; H, 4.57.



product **2**

4a: Pale brown oil, 29% HPLC yield (25% isolated yield); IR (neat) 1758 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (270 MHz, $CDCl_3$) 9.98 (s, 1H, C*H*O), 8.03–7.16 (m, 9H, arom.), 5.35 (s, 2H, $-CH_2-$); MS m/z 264 (M^+).

*2.25. Carbonylation of compound **1b***

According to method A, the carbonylation of **1b** was carried out for 10 h to give products **2b**, **3b** and **4b**.

2b: Pale yellow crystals, 44% HPLC yield (265 mg, 30% isolated yield), mp 196.5–199.0°C; IR (KBr) 3350 cm^{-1} (ν_{OH}), 1750 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.82–7.00 (m, 8H, arom.), 5.37 (d, 1H, $J = 1.9$ Hz, H^c), 5.07 (dd, 1H, $J = 1.9$, 4.9 Hz, H^b), 3.86 (s, 3H, OCH_3), 2.17 (d, 1H, $J = 4.7$ Hz, H^a); MS m/z 294 (M^+). Anal. calc. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.30; H, 4.82.

3b: Yellow oil, 61.7 mg, 7% isolated yield, IR (neat) 1748, 1694 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.99 (s, 1H, C*H*O), 7.68–6.78 (m, 8H, arom.), 5.32 (s, 2H, $-CH_2-$), 3.79 (s, 3H, OCH_3); MS m/z 294 (M^+).

4b: Yellow oil, 45% HPLC yield (353 mg, 40% isolated yield), IR (neat) 1750, 1693 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) 9.94 (s, 1H, C*H*O), 7.98–6.72 (m, 8H, arom.), 5.05 (s, 2H, $-CH_2-$), 3.75 (s, 3H, OCH_3); MS *m/z* 294 (M^+).

2.26. Carbonylation of compound *1c*

According to method A, the carbonylation of **1c** was carried out for 7 h to give products **2c** and **4c**.

2c: Yellow needles, 54% HPLC yield (414 mg, 41% isolated yield), mp 210.3–210.9°C; IR (KBr) 3450 cm^{-1} (ν_{OH}), 1758, 1710 cm^{-1} ($\nu_{C=O}$), ^1H NMR (270 MHz, $CDCl_3$) δ 8.12–7.34 (m, 8H, arom.), 5.39 (d, 1H, $J = 1.9$ Hz, H^c), 5.08 (dd, 1H, $J = 1.9$, 5.0 Hz, H^b), 4.33 (q, 2H, $J = 8.0$ Hz, OCH_2CH$_3$), 2.17 (d, 1H, $J = 4.7$ Hz, H^a), 1.15 (t, 3H, $J = 7.9$ Hz, OCH$_2$CH_3); MS *m/z* 336 (M +). Anal. calc. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79. Found: C, 71.22; H, 4.91.

4c: Yellow oil, 32% HPLC yield (282 mg, 28% isolated yield), IR (neat) 1758, 1702 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) 9.96 (s, 1H, C*H*O), 8.12–7.34 (m, 8H, arom.), 5.11 (s, 2H, $-CH_2-$), 4.10 (q, 2H, $J = 8.4$ Hz, OCH_2CH$_3$), 1.10 (t, 3H, $J = 7.8$ Hz, OCH$_2$CH_3); MS *m/z* 336 (M^+).

2.27. Carbonylation of compound *1d*

According to method A, the carbonylation of **1d** was carried out at 80°C for 30 h to give products **2d**, **3d** and **4d**.

2d: Colorless needle crystals, 50% HPLC yield (248 mg, 41% isolated yield), mp 171.5–172.0°C; IR (KBr) 3291 cm^{-1} (ν_{OH}), 1755 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.65–7.32 (m, 4H, arom.), 5.26 (dq, 1H, $J = 2.0$ Hz, H^c), 4.98 (dd, 1H, $J = 1.3$, 5.8 Hz, H^b), 3.15 (d, 1H, $J = 5.9$ Hz, H^a), 2.08 (d, 3H, $J = 2.0$ Hz. CH_3); MS *m/z* 202 (M^+). Anal. calc. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.15; H, 4.88.

3d: Yellow oil, 11% HPLC yield (42.0 mg, 7% isolated yield), IR (neat) 1755, 1697 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) 10.01 (s, 1H, C*H*O), 8.00–7.30 (m, 4H, arom.), 4.98 (q, 2H, $J = 2.0$ Hz, $-CH_2-$), 2.05 (s, 3H, CH_3); MS *m/z* 202 (M +).

4d: Yellow oil, 34% HPLC yield (121.2 mg, 20% isolated yield), IR (neat) 1752, 1703 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) 9.98 (s, 1H, C*H*O), 8.02–7.30 (m, 4H, arom.), 4.91 (s, 2H, $-CH_2-$), 2.07 (s, 3H, CH_3); MS *m/z* 202 (M^+).

2.28. Carbonylation of compound *1e*

According to method A, the carbonylation of **1e** was carried out for 30 h to give products **2e**, **3e** and **4e**.

2e: Colorless needle crystals, 37% HPLC yield (183 mg, 25% isolated yield), mp 183.0–185.0°C; IR (KBr) 3424 cm^{-1} (ν_{OH}), 1750 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.90–7.40 (m, 4H, arom.), 5.22 (dt, 1H, $J = 2.6$, 1.8 Hz, H^c), 4.95 (dd, 1H, $J = 1.3$, 2.6 Hz, H^b), 3.15 (d, 2H, $J = 1.8$ Hz, CH_2CH$_2$CH$_2$CH$_3$), 2.96 (d, 2H, $J = 1.1$ Hz, H^a), 2.50–1.96 (m, 4H, CH$_2$CH_2CH$_2$CH$_3$), 1.50 (t, 3H, $J = 7.5$ Hz. (CH$_2$)$_3$CH_3); MS *m/z* 244 (M^+). Anal. calc. for $C_{18}H_{14}O_3$: C, 73.75; H, 6.60. Found: C, 73.66; H, 6.49.

3e: Yellow oil, 36.6 mg, 5% isolated yield, IR (neat) 1756, 1699 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 9.98 (s, 1H, C*H*O), 8.16–7.40 (m, 4H, arom.), 5.10 (s, 2H, $-CH_2-$), 2.67–0.90 (m, 9H, CH_2CH_2CH_2CH_3); MS m/z 244 (M^+).

4e: Yellow oil, 52% HPLC yield (329.4 mg, 45% isolated yield), IR (neat) 1756, 1698 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) 9.98 (s, 1H, C*H*O), 8.16–7.30 (m, 4H, arom.), 4.94 (s, 2H, $-CH_2-$), 2.42–0.84 (m, 9H, CH_2CH_2CH_2CH_3); MS m/z 244 (M^+).

*2.29. Carbonylation of compound **1g***

According to method A, the carbonylation of **1g** was carried out for 10 h to give products **2g**, **3g** and **4g**.

2g: Colorless crystals, 18% HPLC yield (92.5 mg, 11% isolated yield), mp 129.3–130.5°C; IR (KBr) 3425 cm^{-1} (ν_{OH}), 1754 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.89–7.31 (m, 9H, arom.), 5.37 (s, 1H, H^c), 2.61 (bs, 1H, H^a), 1.33 (s, 3H, CH_3); MS m/z 278 (M^+). Anal. calc. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.42; H, 5.06.

3g: Colorless crystals, 30% HPLC yield (158.5 mg, 19% isolated yield), mp 142.3–143.5°C; IR (KBr) 1752, 1688 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.89–7.18 (m, 9H, arom.), 5.27 (s, 2H, $-CH_2-$), 2.58 (s, 3H, COCH_3); MS m/z 278 (M^+). Anal. calc. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.56; H, 5.08.

4g: Colorless crystals, 43% HPLC yield (333.6 mg, 40% isolated yield), mp 113.6–114.0°C; IR (KBr) 1748, 1673 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.78–7.29 (m, 9H, arom.), 5.03 (s, 2H, $-CH_2-$), 2.29 (s, 3H, COCH_3); MS m/z 278 (M^+). Anal. calc. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.89; H, 5.08.

*2.30. Carbonylation of compound **1h***

According to method A, the carbonylation of **1h** was carried out for 75 h to give products **3h** and **4h**.

3h: Colorless crystals, 35% HPLC yield (326.4 mg, 32% isolated yield), mp 119.7–120.0°C; IR (KBr) 1746, 1656 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.63–7.26 (m, 14H, arom.), 5.06 (s, 2H, $-CH_2-$); MS m/z 340 (M^+). Anal. calc. for $C_{22}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.02; H, 4.76.

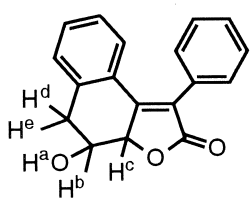
4h: Colorless crystals, 63% HPLC yield (601.8 mg, 59% isolated yield), mp 146.3–148.0°C; IR (KBr) 1753, 1662 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.71–7.22 (m, 14H, arom.), 5.03 (s, 2H, $-CH_2-$); MS m/z 340 (M^+). Anal. calc. for $C_{22}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.11; H, 4.88.

*2.31. Carbonylation of compound **1j***

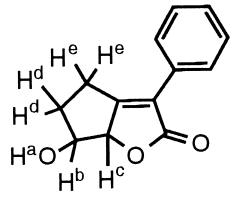
According to method A, the carbonylation of **1j** was carried out for 10 h to give products **2j**, and a mixture of **3j** and **4j**.

2j: Colorless crystals, 63% HPLC yield (333.6 mg, 40% isolated yield), mp 202.5–203.1°C; IR (KBr) 3416 cm^{-1} (ν_{OH}), 1756 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.70–7.09 (m, 9H,

arom.), 4.99 (d, 1H, $J = 10$ Hz, H^c), 4.18 (ddd, 1H, $J = 6.0$, 10.0, 11.0 Hz, H^b), 3.43 (dd, 1H, $J = 6.0$, 11.0 Hz, H^d, H^e), 2.17 (d, 1H, $J = 4.7$ Hz, H^a); MS m/z 278 (M^+). Anal. calc. for $C_{18}H_{14}O_4$: C, 77.68; H, 5.07. Found: C, 77.94; H, 5.02.



2j



2k

*2.32. Carbonylation of compound **1k***

According to method A, the carbonylation of **1k** was carried out for 10 h to give products **2k**, and **3k** and **4k**.

2k: Colorless crystals, 7% HPLC yield (26.0 mg, 4% isolated yield), mp 150.5–152.0°C; IR (KBr) 3453 cm^{-1} (ν_{OH}), 1750 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 7.52–7.38 (m, 5H, arom.), 5.09 (d, 1H, $J = 1.0$ Hz, H^c), 3.67 (m, 1H, H^b), 2.68 (t, 2H, $J = 7.2$ Hz, H^e), 2.20 (d, 1H, $J = 2.3$ Hz, H^a), 1.88 (dt, 2H, $J = 5.2$, 7.4 Hz, H^d); MS m/z 216 (M^+). Anal. calc. for $C_{18}H_{14}O_3$: C, 72.21; H, 5.59. Found: C, 72.30; H, 5.77.

3k: Yellow oil, 28% HPLC yield (78.0 mg, 12% isolated yield); IR (KBr) 1755, 1690 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 9.75 (t, 1H, $J = 1.0$ Hz, C*H*O), 7.47–7.34 (m, 5H, arom.), 4.80 (s, 2H, $-CH_2-$), 2.89 (dt, 2H, $J = 1.0$, 5.6 Hz, CH_2CH_2CHO), 2.73 (t, 2H, $J = 5.5$ Hz, CH_2CH_2CHO); MS m/z 216 (M^+).

4k: Yellow oil, 45% HPLC yield (226.8 mg, 35% isolated yield); IR (KBr) 1758, 1695 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 9.70 (t, 1H, $J = 1.3$ Hz, C*H*O), 7.49–7.30 (m, 5H, arom.), 4.69 (t, 2H, $J = 2.0$ Hz, $-CH_2-$), 2.99 (dt, 2H, $J = 1.3$, 5.9 Hz, CH_2CH_2CHO), 2.77 (dt, 2H, $J = 2.0$, 6.3 Hz, CH_2CH_2CHO); MS m/z 216 (M^+).

*2.33. Carbonylation of compound **1m***

According to method A, the carbonylation of **1m** was carried out for 75 h to give product **2m**.

2m: Pale yellow crystals, 86% HPLC yield (639.3 mg, 73% isolated yield); mp 218.0–218.9°C; IR (KBr) 3503 cm^{-1} (ν_{OH}), 1755, 1698 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 10.8 (s, 1H, C*H*O), 7.83–7.13 (m, 9H, Ph), 5.51 (d, 1H, $J = 5.3$, H^c), 5.20 (dd, 1H, $J = 5.3$, 5.6 Hz, H^b), 3.44 (bs, 1H, H^a); MS m/z 292 (M^+). Anal. calc. for $C_{18}H_{12}O_4$: C, 73.94; H, 4.14. Found: C, 73.70; H, 4.11.

*2.34. Carbonylation of compound **1p***

According to method A, the carbonylation of **1p** was carried out for 15 h to give products **3p** and **4p**.

3p: Pale yellow oil, 39% HPLC yield (31% isolated yield); IR (neat) 1755, 1724 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 8.09–7.17 (m, 9H, arom.), 5.30 (s, 2H, $-CH_2-$), 4.25 (q, 2H, $J = 6.8$ Hz, $CO_2CH_2CH_3$), 1.39 (t, 3H, $J = 7.0$ Hz, $COCH_2CH_3$); MS m/z 308 (M^+).

4p: Pale yellow oil, 59% HPLC yield (48% isolated yield); IR (neat) 1760, 1726 cm^{-1} ($\nu_{C=O}$); ^1H NMR (270 MHz, $CDCl_3$) δ 8.15–7.17 (m, 9H, arom.), 5.19 (s, 2H, $-CH_2-$), 4.26 (q, 2H, $J = 7.1$ Hz, $CO_2CH_2CH_3$), 1.29 (t, 3H, $J = 7.1$ Hz, $CO_2CH_2CH_3$); MS m/z 308 (M^+).

According to method B, the carbonylation of **1p** was carried out for 15 h to give products **5p** and **6p**.

5p: Colorless crystals, 60% yield (69% HPLC yield), mp 172.0–173.0°C; IR (KBr) 1738 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09–7.17 (m, 8H, Ph), 3.80 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 154.0, 141.4, 136.3, 136.2, 135.1, 131.1, 127.6, 127.4, 127.3, 124.8, 122.3, 119.9, 119.0, 115.6, 31.9; MS m/z 234 (M^+). Anal. calc. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.12; H, 4.13.

6p: Yellow oil, 20% yield (28% HPLC yield). IR (KBr) 1727 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.37–7.25 (m, 10H, aromatic ring + $HC=$), 6.89 (d, 1H, $J = 17.2$ Hz, $=CH$), 4.41 (q, 2H, $J = 7.2$ Hz, $CO_2CH_2CH_3$), 1.40 (t, 3H, $J = 7.5$ Hz, $COCH_2CH_3$); MS m/z 252 (M^+).

*2.35. Carbonylation of compound **1q***

According to method B, the carbonylation of **1q** was carried out for 15 h to give products **5q** and **6q**.

5q: Pale yellow crystals, 68% HPLC yield (52% isolated yield), mp 184.0–186.0°C; IR (KBr) 1737 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35–7.15 (m, 7H, aromatic ring), 3.74 (s, 2H, CH_2), 2.44 (s, 3H, $ArCH_3$); MS m/z 246 (M^+). Anal. calc. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.14 H, 4.70.

*2.36. Carbonylation of compound **1r***

According to method B, the carbonylation of **1r** was carried out for 15 h to give products **5r** and **6r**.

5r: Pale yellow crystals, 71% HPLC yield (49% isolated yield), mp 215.0–217.0°C; IR (KBr) 1738 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.33–7.39 (m, 7H, aromatic ring), 3.85 (s, 2H, CH_2), 2.66 (s, 3H, $ArCOCH_3$); MS m/z 276 (M^+).

*2.37. Carbonylation of compound **1s***

According to method B, the carbonylation of **1s** was carried out for 15 h to give products **5s** and **6s**.

5s: Pale yellow crystals, 53% HPLC yield (40% isolated yield), mp 206.0–207.0°C; IR (KBr) 1738 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.36–6.90 (m, 7H, aromatic ring), 3.87 (s, 3H, $ArOCH_3$), 3.73 (s, 2H, CH_2); MS m/z 264 (M^+).

*2.38. Carbonylation of compound **1u***

According to method B, the carbonylation of **1u** was carried out for 60 h to give products **5u** and **6u**.

5u: Pale yellow crystals, 80% HPLC yield (70% isolated yield), mp 175.0–176.0°C; IR (KBr) 1738, 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35–7.40 (m, 7H, aromatic ring), 4.46 (q, 2H, $J = 7.3$ Hz, $CO_2CH_2CH_3$), 4.16 (s, 2H, CH_2), 1.48 (t, 3H, $J = 7.2$ Hz, $COCH_2CH_3$); MS m/z 306 (M^+).

2.39. Carbonylation of compound *1v*

According to method B, the carbonylation of **1v** was carried out for 15 h to give products **5p** and **6v**.

5p: 75% HPLC yield and 64% isolated yield.

6v: Yellow oil, 20% HPLC yield (17% isolated yield); IR (neat) 1727 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.30–7.24 (m, 10H, aromatic ring + –C*H*=CH–), 6.91 (d, 1H, $J = 16.9$ Hz, –CH=C*H*–), 4.06 (s, 3H, CO_2CH_3); MS m/z 238 (M^+).

2.40. Carbonylation of compound *1w*

According to method B, the carbonylation of **1w** was carried out for 20 h to give product **5p** (40% HPLC yield and 30% isolated yield). Product **6w** could not be isolated.

2.41. Carbonylation of compound *1x*

According to method B, the carbonylation of **1x** was carried out for 20 h to give products **5p** (18% HPLC yield) and **6x**.

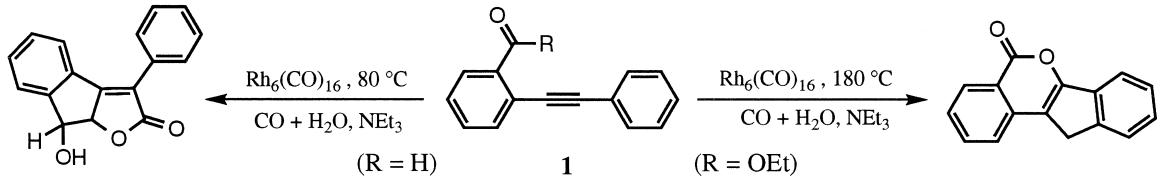
5p: 18% HPLC yield (8% isolated yield).

6x: Yellow oil, 68% HPLC yield (50% isolated yield); IR (neat) 1727 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.37–7.02 (m, 15H, aromatic ring + –C*H*=CH–), 6.82 (d, 1H, $J = 17.0$ Hz, –CH=C*H*–); MS m/z 300 (M^+).

3. Results and discussion

In the course of our study on the carbonylation of alkynes we have now found new types of cyclic carbonylation in which a carbonyl group adjacent to the acetylenic bond takes part in the carbonylation of the acetylenic bond resulting in the formation of a fused lactone derivative. The two novel cyclic carbonylation reactions of alkynes catalyzed by $Rh_6(CO)_{16}$ under the water–gas shift reaction conditions are shown in Eq. (1). One is the formation of a tricyclic lactone, indeno[2,1-*b*]furan **2a**, as a major product from the carbonylation of 2-phenylethynylbenzaldehyde which is an alkyne having a formyl group adjacent to the carbon–carbon triple bond. The other is that ethyl 2-phenylethynylbenzoate having a neighboring ethoxycarbonyl group undergoes simultaneous carbonylation of acetylene, C–H bond activation of the phenyl group and incorporation of the ester group to give a tetracyclic lactone, indeno[1,2-*c*]isocoumarin **5p**. By a close inspection of the structures of **2a** and **5p**, it is clear that in both reactions the cyclic carbonylation of C–C triple bond took place and the

carbonyl group of the formyl as well as ethoxycarbonyl substituents incorporated in the cyclization. Obviously, the two reactions gave different products although they were carried out under the same reaction conditions except the reaction temperature.



2a (major product) **5p** (major product)

(1)

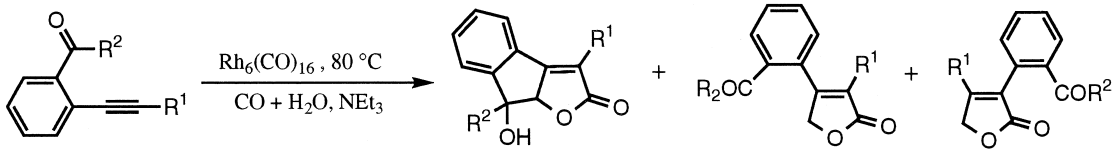
3.1. Rhodium-catalyzed carbonylation of alkynes having a formyl-neighboring group

Alkynes having a functional group are prepared by a coupling reaction between terminal acetylenes and aryl halides which we previously developed by using a CuI–$Pd(PPh_3)_2Cl_2$ catalyst as described in Section 2 [22]. As reported previously [14] the rhodium-catalyzed carbonylation of diphenylacetylene at 80°C gives diphenylfuranone selectively. Similarly a mixture of 2-phenylethynylbenzaldehyde **1a** (3 mmol), Et_3N (3 mmol), H_2O (12 mmol) and $Rh_6(CO)_{16}$ catalyst (0.01 mmol) in chloroform was placed in a 100 ml stainless steel autoclave and stirred under 100 atm of initial carbon monoxide at 80°C for 5 h to give three kinds of products. The major one among the three was isolated by column chromatography on silica gel, recrystallized from ethanol and identified to be 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2*H*-indeno[2,1-*b*]furan **2a**. Two furanones of by-products, **3a** (trace) and **4a** (29% yield), were similarly isolated and identified by the IR, mass, ^1H and ^{13}C NMR, and NOE spectral analyses as well as by the comparison with the spectral data of furanones [14]. The structure of **2a** having the same mass number as **3a** and **4a** was inferred from the analytical and spectral data. Different from **3a** and **4a**, an absorption due to ν(OH) was found around 3540 cm^{-1} in the IR spectrum of **2a**. In addition, a doublet peak assignable to a hydroxyl proton at 3.08 ppm disappeared when a drop of D_2O was added to an NMR sample solution. Finally, the structure of **2a** has been established by an X-ray crystallographic analysis [17] to be a tricyclic skeleton, 2-oxo-3-phenyl-8-hydroxy-8,8a-dihydro-2*H*-indeno[2,1-*b*]furan.

For the carbonylation reaction of **1a**, $[Rh(CO)_2Cl]_2$ and $RhCl_3 \cdot xH_2O$ showed a high catalytic activity while $RhH(CO)(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ gave low conversion of **1a** with a lower selectivity for tricyclic lactone **2a**. Other metal carbonyls such as $Co_2(CO)_8$, $Ru_3(CO)_{12}$ and $Fe(CO)_5$ showed no catalytic activity for the reaction. The selectivity for **2a** is influenced by solvents employed. Dioxane, tetrahydrofuran and chloroform showed good results while benzene, toluene and DMF gave a poor selectivity for **2a**. A temperature in a region of 80–100°C is optimal for the selectivity of **2a**, and the pressure of CO should be higher than 75 atm in order to reach 100% conversion of starting substrate **1a**. The best yield and selectivity for **2a** were attained by use of a $Rh_6(CO)_{16}$ catalyst in chloroform at 80°C under 100 atm of CO.

Results of the carbonylation of alkynes **1a–h** are summarized in Table 1. The reactions of 2-phenylethynylbenzaldehyde derivatives **1b** and **1c** having a substituent at the 4-position of the phenyl group gave the corresponding tricyclic products **2b** and **2c** in 44 and 54% yields, respectively (entries 2 and 3). The carbonylation of 2-(prop-1-ynyl)benzaldehyde **1d** ($R^1 = CH_3$) and 2-(hex-1-ynyl)benzaldehyde **1e** ($R^1 = C_4H_9$) under the same reaction conditions as those of **1a**, however,

Table 1
$Rh_6(CO)_{16}$-catalyzed carbonylation of 2-alkynylbenzaldehydes[a]



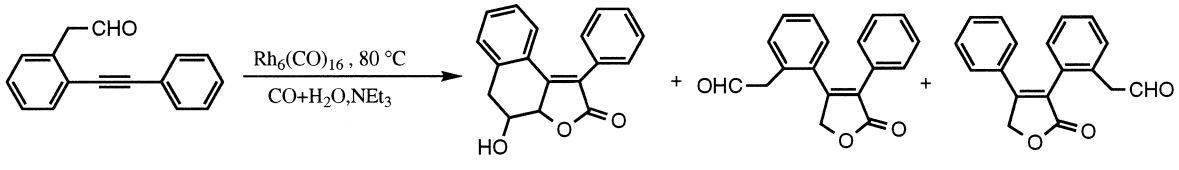
1 **2** **3** **4**

Entry		Alkyne **1**		Reaction time (h)	Yields of products (%)		
		R^1	R^2		**2**	**3**	**4**
1	(**a**)	C_6H_5	H	5	59	trace	29
2	(**b**)	C_6H_4OMe-4	H	10	44	7	45
3	(**c**)	$C_6H_4CO_2Et$-4	H	7	54	trace	32
4	(**d**)	CH_3	H	30	50	11	34
5	(**e**)	C_4H_9	H	40	37	5	52
6	(**f**)	H	H	5	–	–	–
7	(**g**)	C_6H_5	CH_3	45	18	30	43
8	(**h**)	C_6H_5	C_6H_5	75	trace	35	63
9	(**m**)	C_6H_4CHO-2	H	10	86	–	–

[a]The reaction conditions: see Section 2.

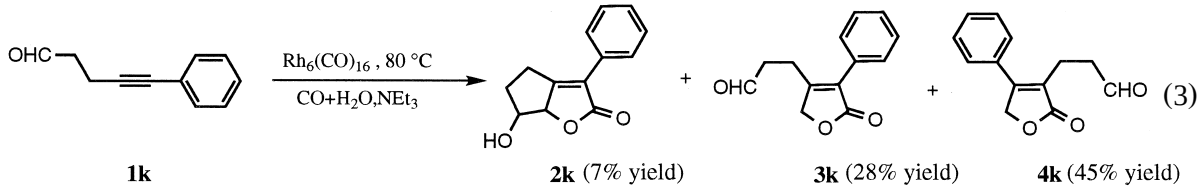
proceeded very slowly (entries 4 and 5). The latter gave a relatively lower selectivity for tricyclic lactone **2e** (37% yield). When a terminal acetylene, 2-ethynylbenzaldehyde **1f**, was applied, the tricyclic lactone was not formed but some oligomers were detected by GPC. It is noteworthy that the reactions of **1a–e** gave furanones **4a–e** in 29–52% yields while only a trace amount of furanones **3a–e** were obtained. Instead of a formyl group, the reaction of alkyne having a keto-neighboring group showed a higher selectivity for furanones **3** and **4**, especially for furanone **3** (entries 7 and 8). The carbonylation of 2-phenylethnylbenzacetophenone **1g** gave the corresponding tricyclic lactone **2g** in 18% yield, and furanones **3g** and **4g** in 30 and 43% yield, respectively. In the reaction of **1h** ($R^1 = C_6H_5$, $R^2 = C_6H_5$), only furanones **3h** and **4h** were obtained although a trace amount of **2h** was detected (entry 8).

We also prepared 2-phenylethynylbenzylaldehyde **1j** and 5-phenyl-4-pentynal **1k** and tried the carbonylation of them. The reaction of **1j** gave a new tricyclic lactone **2j** in 61% yield as a major product along with two isomers of furanones, **3j** and **4j**, as by-products. (Eq. (2)) Although the reaction of 5-phenyl-4-pentynal **1k** afforded furanones **3k** and **4k** as main products, a trace amount of cyclic product **2k** in which the formyl group incorporated was formed. (Eq. (3)) On the other hand, the carbonylation of 2-(2-formylphenyl)ethynylbenzaldehyde **1m** gave tricyclic lactone **2m** in 86% yield with high selectivity. (Table 1, entry 9) In this reaction, no furanones were detected.



1j **2j** (61% yield) **3j** (4% yield) **4j** (20% yield)

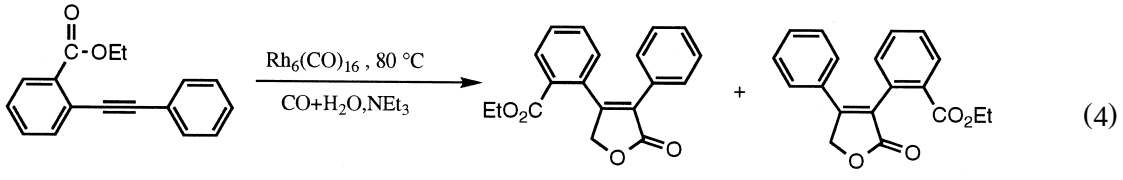
(2)



(3)

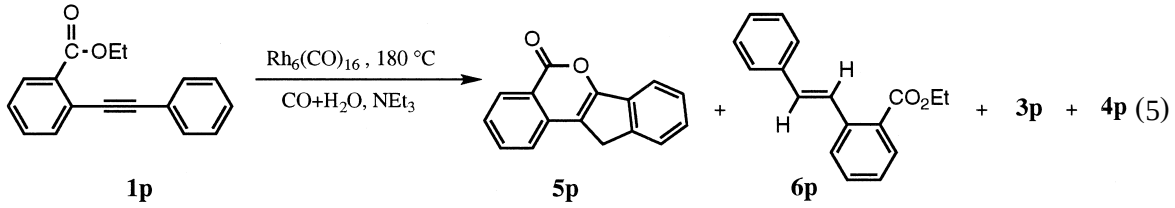
1k **2k** (7% yield) **3k** (28% yield) **4k** (45% yield)

3.2. Rhodium-catalyzed carbonylation of alkynes having an ester-neighboring group



(4)

1p **3p** (39% yield) **4p** (59% yield)



(5)

1p **5p** **6p**

When the reaction of ethyl 2-phenylethynylbenzoate **1p** was carried out under the same reaction conditions as those for 2-phenylethynylbenzaldehyde, two furanone derivatives, 4-(2′-ethoxycarbonyl)phenyl-3-phenylfuran-2(5*H*)-one (**3p**) and 3-(2′-ethoxycarbonyl)phenyl-4-phenylfuran-2(5*H*)-one (**4p**), were obtained. (Eq. (4)) No further cyclization occurred, that is, the ethoxycarbonyl group remained intact. Considering the lower reactivity of an alkoxycarbonyl group in comparison with that of a formyl group, the reaction was performed at a higher temperature, 180°C. As a result, **5p** and **6p** were obtained along with furanones **3p** and **4p**. (Eq. (5)) Product **5p** is a novel indeno[1,2-*c*]isocoumarin derivative, the structure of which was characterized by ^{1}H and ^{13}C NMR, IR, and mass spectra and finally determined by an X-ray crystallographic analysis [18]. Product **6p** is a hydrogenated product of **1p**. In order to improve the selectivity for the new product **5p**, the effect of temperature was investigated. As shown in Table 2, the reactions at a temperature below 120°C gave only furanones **3p** and **4p**. When the temperature was increased to 140°C, **5p** and **6p** were formed and the yields of them increased with the temperature up to 180°C. But no further increase of **5p** was observed even if the reaction was carried out at 200°C. We also examined the effect of additives on the selectivity of **5p**, however, no significant differences in the selectivity were observed on varying amounts or ratios of Et_3N and water. In contrast, the selectivity for **5p** and **6p** was significantly influenced by the concentration of the catalyst, $Rh_6(CO)_{16}$; that is, use of larger amounts of $Rh_6(CO)_{16}$ than 0.3 mol% (based on the substrate) resulted in decreasing yield of **5p**, but increasing amount of hydrogenated product **6p**. Surprisingly, the addition of triphenylphosphine to the reaction system resulted in considerable improvement in the selectivity for **5p** because the formation of

Table 2
Effect of the reaction temperature on the carbonylation of **1p**[a]

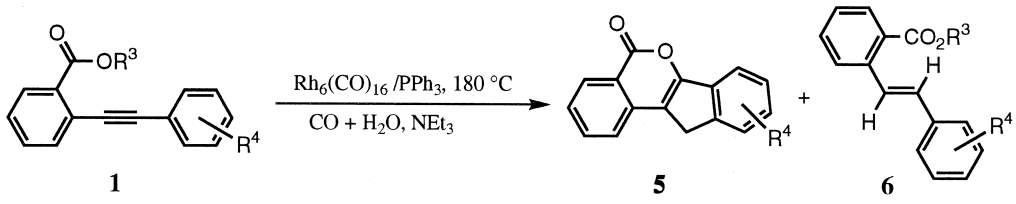
Entry	Rection temperature (°C)	Yields of products (%)			
		3p	**4p**	**5p**	**6p**
1	80	59	39	–	–
2	100	51	44	–	–
3	120	52	45	–	–
4	140	33	35	trace	9
5	160	19	18	34	6
6	180	15	12	45	18
7	200	15	17	43	26

[a]The reaction conditions: see Section 2.

furanones **3p** and **4p** was depressed. On adding PPh_3 at an amount of 20 equivalents to $Rh_6(CO)_6$, **5p** and **6p** were formed in 69 and 28% yield, respectively, and no furanones **3p** and **4p** were detected.

Table 3 summarizes the results of the cyclic carbonylation of several 2-phenylethynylbenzoates under the optimal condition (vide infra). The reactions of 2-phenylethynylbenzoate derivatives **1q**, **1r** and **1s** having a substituent at the 4-position of the phenyl group gave the corresponding indeno[1,2-*c*]isocoumarin derivatives **5q** in 68%, **5r** in 71% and **5s** in 53% yield, along with their hydrogenated products (entries 2, 3 and 4). 2-Phenylethynylbenzoate derivative **1u** having an ethoxycarbonyl group at the 2-position of the phenyl group gave indeno[1,2-*c*]isocoumarin derivative **5u** in high yield (80%, entry 5) although a longer reaction time was required. Methyl 2-phenylethynylbenzoate **1v** gave **5p** in 75% yield, while phenyl 2-phenylethynylbenzoate **1x** afforded **6x** as a major product and **5p** in only 18% yield (entries 7 and 8). Sterically larger esters seem to give lower selectivity for **5**.

Table 3
$Rh_6(CO)_{16}$-catalyzed carbonylation of alkyl 2-phenylethynylbenzoates[a]



1 **5** **6**

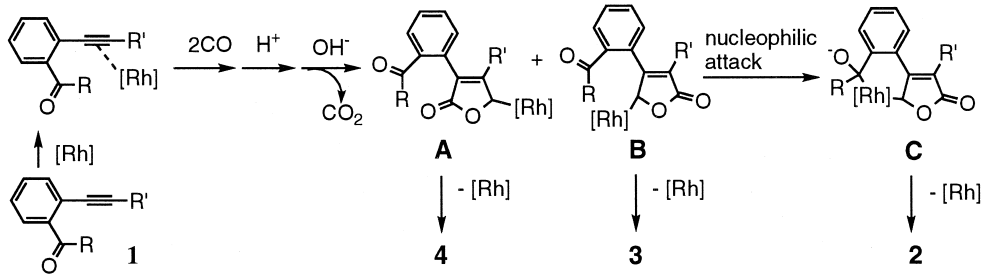
Entry		Alkyne 1		Reaction time (h)	Yields of products(%)	
		R^3	R^4		**5**	**6**
1	(**p**)	C_2H_5	H	15	69	28
2	(**q**)	C_2H_5	*p*-CH_3	15	68	23
3	(**r**)	C_2H_5	*p*-$COCH_3$	15	71	26
4	(**s**)	C_2H_5	*p*-OCH_3	15	53	39
5	(**u**)	C_2H_5	*o*-$CO_2C_2H_5$	60	80	15
6	(**v**)	CH_3	H	15	75	20
7	(**w**)	$CH(CH_3)_2$	H	20	40	–[b]
8	(**x**)	C_6H_5	H	20	18	68

[a]The reaction conditions: see Section 2.
[b]An unidentified complex mixture.

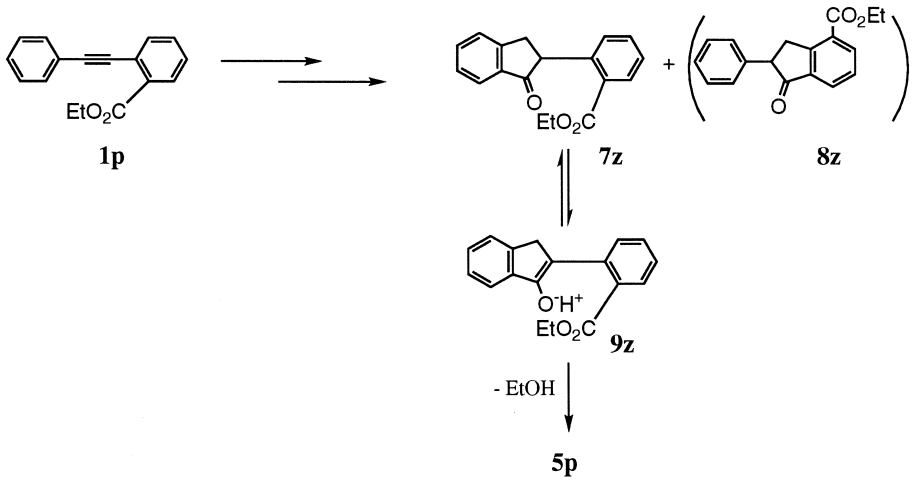
3.3. The reaction mechanism of rhodium-catalyzed carbonylation of alkyne having a carbonyl-neighboring group

Although the mechanisms of the two types of reactions described above are not clear at the present time, it should be of particular interest because they are the first examples where a carbonyl group participates in the carbonylation reaction of alkynes [23,24]. Furthermore, direct formation of novel tricyclic lactone **2** and tetracyclic lactone **5** from alkynes should be noteworthy. Based on the previously proposed mechanism for the formation of 2(5*H*)-furanones from alkynes [14], a plausible mechanism of the formation of tricyclic lactone **2** is tentatively proposed in Scheme 1. A rhodium complex formed by the coordination of alkyne undergoes insertion of two molecules of CO followed by the attack of H^+ and OH^-, yielding two precursors, **A** and **B**. Accompanied with elimination of [Rh] from precursors **A** and **B**, furanones **3** and **4** may be formed as proposed previously [14]. Since in precursor **B** the rhodium is situated at the position near to the formyl group, a nucleophilic attack of the rhodium to the carbonyl group of the formyl substituent (R = H) will result in the formation of intermediate **C** leading to **2** (Scheme 1). We have some experimental results supporting this proposed reaction pathway. In our previous report of furanone synthesis from alkynes, two structural isomers of furanones like **3** and **4** were obtained in the ratio of about 50:50 [14]. As shown in Table 1, the reactions of alkynes **1a–e** yielded products **2** and **4** while only a trace amount of product **3** was obtained. In contrast, the reactions of 2-phenylethynylbenzacetophenone **1g** ($R = CH_3$) and 2-phenylethynylbenzbenzophenone **1h** ($R = C_6H_5$) gave a significant amount of furanone **3** with a trace amount of **2**. These facts strongly suggest that **B** may be a common precursor of both **2** and **3**.

The reaction of **1p** ($R = OC_2H_5$) under the same condition gave furanones **3p** and **4p** without formation of product **2p**. On the other hand, the reaction at a higher temperature of 180°C resulted in the formation of **5p** and **6p**. In separate experiments, the reaction of **1p** at 80°C for 10 h and then at 180°C for 10 h did not afford tetracyclic lactone **5p**, but only furanones **3p** and **4p** were obtained as products in a total yield of 80%, indicating that the present novel cyclic carbonylation proceeds via neither furanone **3** nor **4**. These facts suggest the active rhodium species in the present cyclic carbonylation at 180°C may be different from that at 80°C. Formation of **5p** can be accounted for by elimination of the ethoxy group from the starting substrate **1p** and addition of one molecule each of carbon monoxide and hydrogen to **1p**. The elimination of the ethoxy group from **1p** was confirmed by observing the formation of ethanol after the reaction. An experiment employing D_2O instead of H_2O indicated that the hydrogen comes from water. Thus, the tetracyclic skeleton of **5p** must be built up by the carbonylation of **1p** accompanied by C–O bond fission of the ester group and C–H bond activation of the phenyl group.

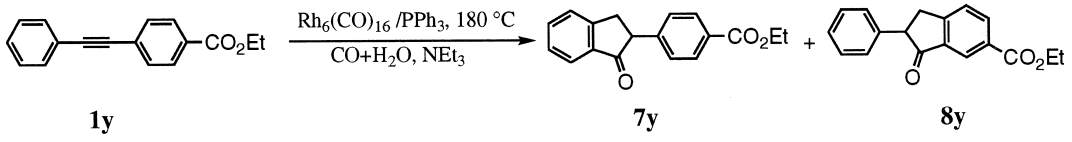


Scheme 1.



Scheme 2.

An additional experiment of the carbonylation of ethoxy *p*-phenylethynylbenzoate **1y** was carried out under the same condition as that of **1p**. Two kinds of indanones **7y** and **8y** were obtained as major products with a ratio of about 50:50. (Eq. (6)) This phenomenon provides valuable information on the reaction mechanism of **1p**, that is, the reaction performed at 180°C may firstly produce the indanone derivative **7z**, which may be in an equilibrium with the corresponding enolate intermediate **9z**. (Scheme 2) When the ester group is adjacent to the enolate group, intra-molecular ester exchange would occur with an elimination of ethanol to give tetracyclic lactone **5p**. On the other hand, as compared to the reaction 6 where indanone **8y** was obtained, indanone **8z** has not been detected in the reaction of **1p**. This might be due to the highly selective formation of **7z** when the ester group is at an *ortho*-position to the acetylene triple bond although the reason is not clear at present why the *ortho*-ester group effectively assists the selective formation of **7z**. Further studies are now in progress to clarify the mechanism of the present reactions.



(6)

4. Conclusion

The carbonylation of 2-phenylethynylbenzaldehyde catalyzed by $Rh_6(CO)_{16}$ under water–gas shift reaction conditions gave a tricyclic lactone, indeno[2,1-*b*]furan. The similar reaction of 2-phenylethynylbenzoate afforded an isomeric mixture of furanone derivatives, however, use of a higher reaction temperature resulted in the formation of tetracyclic lactone, indeno[1,2-*c*]isocoumarin. In these reactions, cyclic carbonylation of the alkynes occurred and at the same time the carbonyl group of formyl and alkoxycarbonyl substituents adjacent to the carbon–carbon triple bond participated in the cyclization. The present reactions provide the convenient method for the synthesis of tricyclic and

tetracyclic ring systems directly from acetylenic substrates which are easily prepared by a palladium-catalyzed cross-coupling of aryl halides with terminal alkynes [22].

Acknowledgements

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