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Palladium-catalyzed 1,6- and 1,5-diyne-carbon monoxide reaction for preparation of alkylidenecyclopentenones and -butenolides

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Abstract

Carbonylative [2 + 2 + 1] cycloaddition of 1,6-diyne under carbon monoxide at atmospheric pressure catalyzed by $Pd_2(dba)_3$-PPh_3-CF_3SO_3H presents a new approach to the formation of a bicyclo[3.3.0]octa-1,5-dien-3-one ring system. Under higher pressure the reaction of 1,6- and 1,5-diynes occurred in a different fashion via tandem insertion of carbon monoxide to yield alkylidenebutenolide.

Keywords: Cyclocarbonylation; Palladium; 1,6-Diyne; Alkylidenecyclopentenone; Alkylidenebutenolide

1. Introduction

Transition metal-mediated or -catalyzed cyclocarbonylation of 1,6-diynes, 1,6-enynes, and allenynes has been proved useful for the synthesis of bicyclooctanones, bicyclooctenones [1], and 4-alkylidenecyclopentenones [2] of medical and theoretical interests [3]. The representative is the Pauson–Khand reaction, that is, [2 + 2 + 1] cyclocarbonylation reaction of 1,6-enyne to furnish a bicyclo[3.3.0]octenone framework. Cyclocarbonylation of 1,6-diynes mediated by transition metal complexes appears as a potentially useful reaction for the preparation of cyclopentadienones fused to five-membered rings. In most cases, however, reactions cannot be catalytic because the products are obtained as η^4-metal complexes [4]. Demetalation steps are required to generate uncomplexed products. A few catalytic cyclocarbonylation reactions of 1,6-diynes have been reported. Chung et al. reported cobalt-catalyzed tandem cycloaddition reaction of 1,6-diynes with diynes or alkynes under carbon monoxide to afford substituted bicyclooctenones [5]. Iridium complex-catalyzed carbonylative cyclization of 1,6-diynes to provide cyclopentadienones has been reported by Shibata et al. [6]. Sugihara et al. demonstrated that methylidynetricobalt nonacarbonyl could be used as catalyst for the reaction of 1,6-diynes and carbon monoxide to produce cyclopentadienones [7]. The reactions of 1,6-diynes with silanes under carbon monoxide pressure via rhodium-catalyzed silylcarbobicyclization opened a novel route to 2-silylbicyclo[3.3.0]octenones [8] and 2-silylbicyclo[3.3.0]octa-1,5-dien-3-ones [9]. Ruthenium-catalyzed reaction of 1,6-diynes with hydrosilanes and carbon monoxide presented a new mode of carbon monoxide incorporation giving rise to catechol derivatives [10]. Palladium complexes have seldom been utilized for this type of cyclization [11] despite the rich chemistry of palladium-catalyzed alkyne-carbon monoxide reaction in alcohol

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(alkoxycarbonylation) [12]. In this paper, we wish to report the palladium-catalyzed reactions of 1,6-diynes with carbon monoxide under the normal pressure leading to the formation of bicyclo[3.3.0]octa-1,5-dien-3-ones. We have also found that under higher pressure the reaction of 1,6- and 1,5-diynes takes place in a different fashion via tandem insertion of carbon monoxide to generate alkylidenebutenolides.

2. Experimental

2.1. Materials

Diynes **1** and **4** were synthesized according to the standard methods described in a literature [13]. Thus, **1a**, **1b**, **1c**, **1f**, **1j**, and **4** were prepared from the corresponding diynes and appropriate alkyl iodides or methyl chloroformate. **1d** and **1i** were synthesized by coupling reaction of the corresponding diynes with iodobenzene in the presence of a $PdCl_2(PPh_3)_2$-CuI catalyst. **1g** and **1h** were synthesized from diethyl malonate and appropriate 2-alkynyl *p*-toluenesulfonate. **1e** was prepared from 1,6-nonadiyne and iodobenzene in the presence of a $PdCl_2(PPh_3)_2$-CuI catalyst. 1,6-Nonadiyne was obtained from 1-trimethylsilyl-1,6-nonadiyne and KF. The silyldiyne was prepared from trimethylsilylacetylene and 7-iodo-3-heptyne, which was prepared from the corresponding tosylate and NaI. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 or a DPX-400 in $CDCl_3$ as solvent. GC–MS analyses were performed on a Shimadzu GCMS-QP 2000. IR spectra were recorded with a JEOL FT/IR-350. GC analyses were carried out with a Shimadzu GC-8A. Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. The products **3a** and **5** were not sufficiently stable for elemental analysis.

2.2. Reaction

2.2.1. General procedure for the reaction of diyne *1* with carbon monoxide

$Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg; 0.025 mmol), PPh_3 (0.05 or 0.1 mmol), and $ClCH_2CH_2Cl$ (3 ml) were added in a 50 ml stainless steel autoclave and the mixture was stirred for 10 min. After CF_3SO_3H (30.0 mg; 0.2 mmol) was added, the mixture was stirred for additional 20 min. Then diyne **1** (0.5 mmol) was added and the autoclave was pressurized to 1 atm by introducing carbon monoxide. The autoclave was heated in an oil bath at 80 °C for 1 h. The reaction mixture was allowed to cool to room temperature and the carbon monoxide was released carefully. The crude reaction mixture was diluted with ether, filtered through a plug of silica gel. After the organic layer was washed with water, the crude product was concentrated in vacuo and purified by flash chromatography on silica gel eluting with hexane/ethyl acetate.

*2.2.1.1. 2,4-Diethylbicyclo[3.3.0]octa-1,5-dien-3-one (**2a**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.99 (dd, 1H, J = 2.5, and 2.0 Hz), 2.87–2.86 (m, 2H), 2.78–2.76 (m, 2H), 2.70–2.68 (m, 1H), 2.28 (q, 2H, J = 7.6 Hz), 1.91–1.83 (m, 1H), 1.56–1.50 (m, 1H), 1.09 (t, 3H, J = 7.6 Hz), 0.93 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 210.3, 179.9, 149.2, 134.3, 127.9, 47.0, 36.0, 24.9, 22.9, 17.3, 12.2, 11.3. IR (neat): 1697, and 1629 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 133, 148, 176 (M^+). Anal. calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.51; H, 8.98%.

*2.2.1.2. 2,4-Dimethylbicyclo[3.3.0]octa-1,5-dien-3-one (**2b**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.95 (t, 1H, J = 2.5 Hz), 2.85–2.84 (m, 2H), 2.76 (q, 1H, J = 7.6 Hz), 2.72–2.71 (m, 2H), 1.79 (s, 3H), 1.22 (d, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 209.21, 178.20, 148.69, 125.83, 125.56, 38.32, 33.70, 22.77, 12.30, 6.86. IR (neat): 1699, 1635, 1446, 1316, and 1001 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 91, 105, 148 (M^+). Anal. calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.46; H, 8.38%.

*2.2.1.3. 2,4-Dipropylbicyclo[3.3.0]octa-1,5-dien-3-one (**2c**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.97 (t, 1H, J = 2.5 Hz), 2.86–2.85 (m, 2H), 2.75–2.73 (m, 3H), 2.22 (t, 2H, J = 7.6 Hz), 1.83–1.74 (m, 1H), 1.52 (q, 2H, J = 7.6 Hz), 1.47–1.35 (m, 3H), 0.92 (t, 3H, J = 7.3 Hz), 0.90 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 210.57, 180.30, 149.42, 132.67, 128.04, 45.66, 35.92, 32.01, 26.01, 24.95, 21.02, 20.39, 14.15, 14.12. IR (neat): 1697, 1629, 1458, and 1315 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 133, 162, 204 (M^+). Anal.

calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.83; H, 10.07%.

*2.2.1.4. 2,4-Diphenylbicyclo[3.3.0]octa-1,5-dien-3-one (**2d**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.87 (d, 2H, $J = 8.2$ Hz), 7.40 (t, 2H, $J = 8.2$ Hz), 7.34–7.23 (m, 6H), 6.21 (t, 1H, $J = 2.8$ Hz), 4.14 (s, 1H), 3.19–3.18 (m, 2H), 3.03–3.02 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 205.22, 181.23, 148.85, 137.01, 132.47, 128.71, 128.53, 128.45, 128.20, 127.66, 127.60, 127.12, 52.41, 36.20, 27.86. IR (neat): 1695, 1597, 1494, 1126, 722, and 694 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 243, 272 (M^+). Anal. calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.68; H, 5.58%.

*2.2.1.5. 4-Ethyl-2-phenylbicyclo[3.3.0]octa-1,5-dien-3-one (**2e**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.83 (d, 2H, $J = 7.7$ Hz), 7.40 (t, 2H, $J = 7.7$ Hz), 7.29–7.25 (m, 1H), 6.21 (t, 1H, $J = 2.7$ Hz), 3.08–3.06 (m, 2H), 2.97–2.96 (m, 2H), 2.89–2.87 (m, 1H), 1.97–1.95 (m, 1H), 1.68–1.61 (m, 1H), 0.99 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$): δ 208.51, 180.76, 149.20, 132.69, 130.81, 129.42, 128.40, 127.57, 127.40, 47.67, 36.27, 27.52, 23.14, 11.30. IR (neat): 1686, 1596, 1492, 1444, 1325, 1149, and 755 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 165, 196, 224 (M^+). Anal. calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.07; H, 7.53%.

*2.2.1.6. 7,7-Diethoxycarbonyl-2,4-dimethylbicyclo-[3.3.0]octa-1,5-dien-3-one (**2g**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.00 (s, 1H), 4.28–4.21 (m, 4H), 3.41–3.30 (m, 2H), 2.87 (q, 1H, $J = 7.6$ Hz), 1.82 (s, 3H), 1.29 (dt, 6H, $J = 1.0$, and 7.0 Hz), 1.25 (d, 3H, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 209.22, 173.80, 169.96, 169.82, 153.21, 131.11, 123.51, 119.64, 69.40, 62.22, 40.30, 33.24, 14.09. IR (neat): 1725, 1702, 1644, 1236, 1177, 1125, 1046, and 853 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 191, 219, 292 (M^+). Anal. calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.51; H, 7.02%.

*2.2.1.7. 7,7-Diethoxycarbonyl-2,4-diethylbicyclo-[3.3.0]octa-1,5-dien-3-one (**2h**).* Colorless oil. ^{1}H NMR ($CDCl_3$): 6.02 (s, 1H), 4.26–4.22 (m, 4H), 3.41 (s, 2H), 2.81–2.80 (m, 1H), 2.30 (q, 2H, $J = 7.6$ Hz), 1.92–1.84 (m, 1H), 1.66–1.57 (m, 1H), 1.31–1.27 (m, 6H), 1.12 (t, 3H, $J = 7.6$ Hz), 0.92 (t, 3H, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 208.53, 173.60, 169.94, 151.95, 137.50, 123.80, 69.80, 62.21, 62.17, 46.89, 33.51, 22.52, 17.44, 14.09, 14.06, 11.90, 10.93. IR (neat): 1734, 1706, 1459, 1256, 1178, 1060, and 846 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 247, 320 (M^+). Anal. calcd. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.31; H, 7.25%.

*2.2.1.8. 7,7-Diethoxycarbonyl-2,4-diphenylbicyclo-[3.3.0]octa-1,5-dien-3-one (**2i**).* The mp 98.6–99.0 °C ^{1}H NMR ($CDCl_3$): 7.83 (d, 2H, $J = 8.2$ Hz), 7.41 (t, 2H, $J = 7.6$ Hz), 7.34–7.31 (m, 3H), 6.23 (s, 1H), 4.30–4.22 (m, 5H), 3.86–3.76 (m, 2H), 1.32–1.26 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 203.53, 174.76, 169.62, 169.47, 151.10, 135.89, 131.38, 131.02, 128.81, 128.61, 128.53, 128.46, 128.19, 128.03, 127.81, 127.41, 69.83, 65.90, 62.46, 52.20, 35.93, 14.12, 14.09. IR (KBr): 1731, 1718, 1600, 1252, 1179, 1063, and 726 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 241, 343, 416 (M^+). Anal. calcd. for $C_{26}H_{24}O_5$: C, 74.98; H, 5.81. Found: C, 74.68; H, 5.95%.

*2.2.1.9. 7,9-Diethylbicyclo[4.3.0]nona-1,6-dien-8-one (**2j**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.90 (t, 1H, $J = 4.3$ Hz), 2.71–2.55 (m, 3H), 2.29 (q, 2H, $J = 5.3$ Hz), 2.24 (q, 2H, $J = 7.5$ Hz), 1.90–1.67 (m, 4H), 1.01 (t, 3H, $J = 7.5$ Hz), 0.80 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$): δ 208.09, 163.39, 139.98, 123.10, 47.91, 25.21, 24.39, 22.83, 22.19, 16.17, 12.95, 6.71. IR (neat): 1693, 1614, 1458, and 1038 cm^{-1}. GC-MS (EI, 70 eV): *m/e*: 133, 162, 190 (M^+). Anal. calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.07; H, 9.75%.

2.2.2. Reaction of 3-hexyne with carbon monoxide

$Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg; 0.025 mmol), PPh_3 (26.2 mg; 0.1 mmol), and $ClCH_2CH_2Cl$ (3 ml) were added in a 50 ml stainless steel autoclave and the mixture was stirred for 10 min. After CF_3SO_3H (30.0 mg; 0.2 mmol) was added, the mixture was stirred for additional 20 min. 3-Hexyne (53.1 mg; 0.65 mmol) was added and the autoclave was pressurized to 1 atm by introducing carbon monoxide. The autoclave was heated in an oil bath at 100 °C for 12 h. The reaction mixture was allowed to cool to room temperature and the carbon monoxide was released carefully. The crude reaction mixture was diluted with ether, filtered through a plug of silica gel. After the organic layer

was washed with water, the crude product was concentrated in vacuo and purified by flash chromatography on silica gel eluting with hexane/ethyl acetate (10/1) to give (*Z*)-2,3,5-triethyl-4-ethylidenecyclopent-2-enone (24.9 mg; 0.13 mmol; 40%).

2.2.2.1. (Z)-2,3,5-Triethyl-4-ethylidenecyclopent-2-enone. Colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.82 (dq, 1H, J = 1.4, and 7.2 Hz), 2.90 (t, 1H, J = 4.5 Hz), 2.50 (q, 2H, J = 7.7 Hz), 2.31–2.21 (m, 2H), 1.99–1.94 (m, 1H), 1.85 (d, 3H, J = 7.2 Hz), 1.83–1.75 (m, 1H), 1.14 (t, 3H, J = 7.6 Hz), 1.02 (t, 3H, J = 7.6 Hz), 0.68 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 208.54, 168.61, 142.56, 140.39, 118.79, 46.93, 22.51, 19.09, 16.58, 14.96, 13.93, 13.41, 8.49. IR (neat): 1696, 1604, 1458, and 1056 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 135, 164, 192 (M^+). Anal. calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.87; H, 10.83%.

*2.2.3. Reaction of **1a** with carbon monoxide under higher pressure*

$Pd_2(dba)_3{\cdot}CHCl_3$ (25.9 mg; 0.025 mmol), PPh_3 (0.05 or 0.1 mmol), and $ClCH_2CH_2Cl$ (3 ml) were added in a 50 ml stainless steel autoclave and the mixture was stirred for 10 min. After CF_3SO_3H (30.0 mg; 0.2 mmol) was added, the mixture was stirred for additional 20 min. Diyne **1a** (0.5 mmol) was added and the autoclave was pressurized to 50 atm by introducing carbon monoxide. The autoclave was heated in an oil bath at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature and the carbon monoxide was released carefully. The crude reaction mixture was diluted with ether, filtered through a plug of silica gel. After the organic layer was washed with water, the crude product was concentrated in vacuo and purified by flash chromatography on silica gel eluting with hexane/ethyl acetate. The yield of **3a** was determined by GC to be 13%.

*2.2.3.1. 7-Ethyl-9-oxa-2-(1-propenyl)bicyclo[4.3.0]-nona-1,6-dien-8-one (**3a**).* Colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.66 (dt, 1H, J = 15.7, and 0.9 Hz), 5.98 (dq, 1H, J = 15.7, 6.9 Hz), 2.60 (t, 2H, J = 6.4 Hz), 2.42 (t, 2H, J = 6.1 Hz), 2.34 (q, 2H, J = 7.6 Hz), 1.90–1.86 (m, 5H), 1.13 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 170.65, 148.10, 144.52, 130.17, 125.47, 124.31, 118.94, 23.74, 22.59, 22.30, 19.02, 17.16, 12.74. IR (neat): 2935, 1751, 1647, 1626, 1439, 1227, 1027, and 933 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 204 (M^+).

*2.2.4. Reaction of **4** with carbon monoxide*

$[Pd(PPh_3)_2(MeCN)_2]$ (44.3 mg; 0.025 mmol) and acetonitrile (3 ml) were added in a 50 ml stainless steel autoclave. After the mixture was stirred for 10 min, diyne **4** (0.5 mmol) was added and the autoclave was pressurized to 50 atm by introducing carbon monoxide. The autoclave was heated in an oil bath at 80 °C for 1 h. The reaction mixture was allowed to cool to room temperature and the carbon monoxide was released carefully. The crude reaction mixture was diluted with ether, filtered through a plug of silica gel. The crude product was concentrated in vacuo and purified by flash chromatography on silica gel eluting with hexane/ethyl acetate. The yield of **5** was determined by GC to be 48%.

*2.2.4.1. 7,8-Benzo-2-ethyl-4-oxa-6-(1-propenyl)-bicyclo[3.3.0]octa-1,5-dien-3-one (**5**).* Red oil: This compound is unstable and decomposes within a day. ^{1}H NMR ($CDCl_3$): δ 7.33 (d, 1H, J = 7.2 Hz), 7.18 (t, 1H, J = 7.2 Hz), 7.15 (d, 1H, J = 7.2 Hz), 7.04–7.00 (m, 1H), 6.53 (dq, 1H, J = 15.8, and 6.8 Hz), 6.20 (dq, 1H, J = 15.8, and 1.8 Hz), 2.62 (q, 2H, J = 7.6 Hz), 1.95 (dd, 3H, J = 1.8, 6.8 Hz), 1.30 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 173.33, 150.55, 150.13, 145.97, 135.93, 131.03, 127.91, 126.34, 125.62, 124.82, 120.67, 119.01, 114.18, 19.68, 18.73, 12.97. IR (neat): 1774, 1634, 1442, 1246, 921, and 733 cm^{-1}. GC–MS (EI, 70 eV): *m/e*: 195, 167, 152, 238 (M^+).

3. Results and discussion

In initial experiments aimed at developing palladium-catalyzed cyclocarbonylation, we employed 3,8-undecadiyne (**1a**) for the substrate as probe. The results are given in Table 1. The reaction of **1a** with carbon monoxide (1 atm) at 80 °C for 1 h catalyzed by $Pd_2(dba)_3{\cdot}CHCl_3$-PPh_3 (PPh_3/Pd = 1; dba = dibenzylideneacetone) in 1,2-dichloroethane did not give any carbonylated products (entry 1). Considering the important role of an acid played in

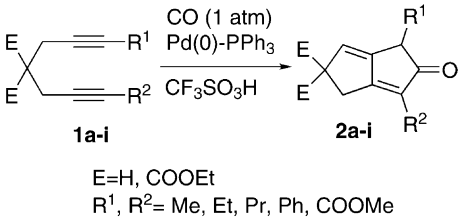
Table 1
Palladium-catalyzed cyclocarbonylation of **1a**[a]

Entry	Acid	pk_a	CO (atm)	Yield of **2a** (%)[b]
1	–	–	1	0
2	CH_3COOH	4.7	1	0
3	4-$CF_3C_6H_4COOH$	–	1	1
4	CF_3COOH	0.23	1	Trace
5	CH_3SO_3H	−1.2	1	12
6	4-$CH_3C_6H_4SO_3H$	−2.2	1	17
7	4-$ClC_6H_4SO_3H$	–	1	14
8	HBF_4·Et_2O	–	1	14
9	CF_3SO_3H	−5.2	0.5	15
10	CF_3SO_3H	–	1	72 (80)[c]
11	CF_3SO_3H	–	2	47
12	CF_3SO_3H	–	5	34

[a] **1a**: 0.5 mmol, $Pd_2(dba)_3$·$CHCl_3$: 0.025 mmol, PPh_3: 0.05 mmol, acid: 0.2 mmol, $ClCH_2CH_2Cl$: 3 ml; 80 °C, 1 h.
[b] GC yield based on **1a** charged.
[c] PPh_3: 0.1 mmol.

alkoxycarbonylation of alkynes catalyzed by palladium complexes [12], we investigated the effects of acids on the cyclocarbonylation of **1a**. Weaker acids like acetic or sulfonic acids were inefficient (entries 2–7). The addition of a catalytic amount of a stronger acid, i.e. trifluoromethanesulfonic acid (acid/Pd = 4), proved to provide the most efficient catalytic system producing the alkylidenecyclopentenone, 2,4-diethylbicyclo[3.3.0]octa-1,5-dien-3-one (**2a**), in a fair yield of 72% (entry 10) (Eq. (1)). The yield of **2a** increased slightly to 80% with increasing PPh_3 added (PPh_3/Pd = 2). Among the ligands tested (such as P(*o*-tol)$_3$, P(OPh)$_3$, P(2,6-dimethoxyphenyl)$_3$, P(Bu^n)$_3$, P(2-furyl)$_3$, (2-pyridyl)PPh_2, $AsPh_3$, dppe, dppp, and dppf), triphenylphosphine was turned out to be most effective. Although (2-pyridyl)PPh_2-Pd(II)-acid system was developed as a highly efficient catalyst for methoxycarbonylation of propyne [14], the phosphine was not so effective for this cyclocarbonylation. The variation of carbon monoxide pressure also affected the yield of **2a**. Lower or higher pressure of carbon monoxide than 1 atm decreased **2a** in the yield significantly (entries 9, 11, and 12).

Then the conditions for the cyclocarbonylation of 1,6-diyne were fixed (Pd/PPh_3/CF_3COOH = 1/2/4) and were applied to various substrates (Scheme 1). The results are given in Table 2. The reaction proceeded fairly where the substituent groups on the triple bonds were electron donating as is shown in



Scheme 1. Cyclocarbonylation of 1,6-diyne **1**.

entry 2 (Me) or entry 3 (Pr). The reaction of an unsymmetrical 1,6-diyne with R^1 = Et and R^2 = Ph provided unsymmetrical bicyclooctadienone **2e** regioselectively albeit in modest yield (entry 5). Unfortunately, another unsymmetrical 1,6-diyne bearing Et and COOMe groups on the respective triple bond did not give the expected product appreciably. In the case where R^1 and R^2 were COOMe, the yield declined (entry 6). Rather low yields were obtained generally with the malonate-based substrates (entries 7–9) indicating that the nature of the ethoxycarbonyl group at the C-4 position of 1,6-diynes also exerted appreciable effects on the reaction. Attempts to use 1,6-diynes containing a terminal alkyne group were unsuccessful. In contrast to the internal 1,6-diynes, they were consumed by side reactions, e.g. oligomerization. In order to explore the scope, a 1,7-diyne compound, i.e. 3,9-dodecadiyne (**1j**), was subjected to the reaction. This diyne produced the corresponding cyclopentenone **2j** fused to a six-membered ring however, the yield was disappointingly low at 11%.

Table 2
Cyclocarbonylation of 1,6-diyne **1**[a]

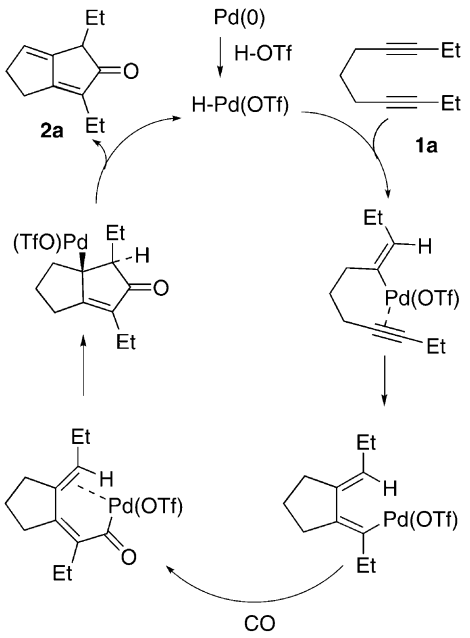
Entry	**1**				2	
		E	R^1	R^2	Yield (%)[b]	
1	**1a**	H	Et	Et	**2a**	80[c]
2	**1b**	H	Me	Me	**2b**	52
3	**1c**	H	Pr	Pr	**2c**	76
4	**1d**	H	Ph	Ph	**2d**	20
5	**1e**	H	Et	Ph	**2e**	30
6	**1f**	H	COOMe	COOMe	**2f**	Trace
7	**1g**	COOEt	Me	Me	**2g**	33
8	**1h**	COOEt	Et	Et	**2h**	51
9	**1i**	COOEt	Ph	Ph	**2i**	27

[a] **1**: 0.5 mmol, $Pd_2(dba)_3$·$CHCl_3$: 0.025 mmol, PPh_3: 0.1 mmol, CO: 1 atm, CF_3SO_3H: 0.2 mmol, $ClCH_2CH_2Cl$: 3 ml; 80 °C, 1 h.
[b] Isolated yield based on **1** charged.
[c] GC yield.

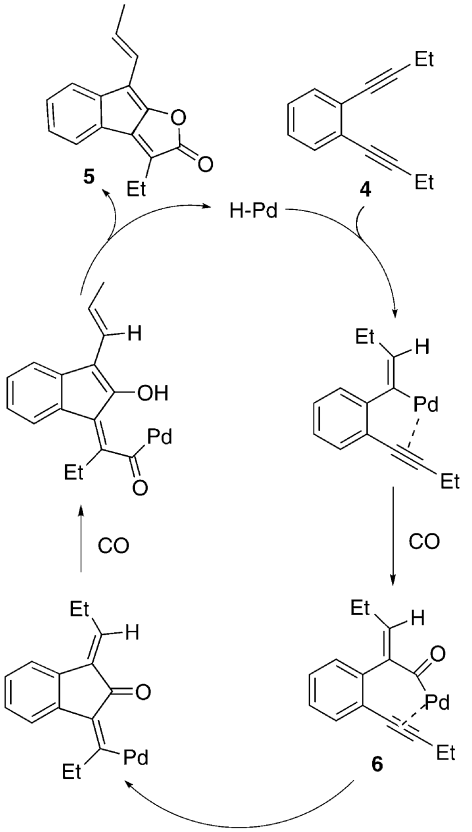
In order to expand the scope, the intermolecular version of this chemistry was also investigated. When 3-hexyne was allowed to react with carbon monoxide under the slightly severe reaction conditions (1 atm, 100 °C) for 12 h, (*Z*)-2,3,5-triethyl-4-ethylidenecyclopent-2-enone was obtained in an isolated yield of 40%, stereoselectively (Eq. (2)). The *Z* stereochemistry around the exo double was determined by an NOE experiment. Vinylic trifluoromethanesulfonate was a remarkable byproduct resulting from the coupling reaction of the alkyne with the acid.

Usually, carbon monoxide pressure of 1 atm was employed for the cyclocarbonylation reaction of **1a**. Further studies on the effects of the pressure on the cyclocarbonylation reaction revealed a dramatic change of the reaction course. As the pressure was increased, the yield of ketone **2a** decreased (vide supra), and a new product based on the tandem carbon monoxide insertion was emerged. Thus, the reaction of **1a** at 80 °C under 50 atm of carbon monoxide pressure produced butenolide **3a** fused to a six-membered ring in 13% yield after 12 h without concomitant formation of **2a** (Eq. (3)). In spite of the intensive studies, the yield of **3a** did not increase significantly. The low yield of **3a** may be partially accounted for the low stability of the compound under the reaction conditions. Consequently, we turned our attention to a 1,5-diyne substrate which should give rise to a butenolide fused to a five-membered ring. A candidate may be *o*-di(1-butynyl)benzene (**4**). Unfortunately, this diyne afforded no cyclocarbonylation products under 50 atm at 80 °C with the catalytic system of $Pd_2(dba)_3$-PPh_3-CF_3SO_3H. Pursuing an effective catalyst, we found eventually that a cationic palladium complex, $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$, was capable of cyclocarbonylating **4** even in the absence of the co-catalyst CF_3SO_3H to afford butenolide **5** in 48% yield at 80 °C after 1 h in acetonitrile (Eq. (4)). The cationic complex also effected the cyclocarbonylation of 1,6-diyne **1a** under 1 atm in acetonitrile. However, the yield of **2a** was rather low even under forced conditions (0%, 80 °C, 1 h; 21%, 80 °C, 12 h; 27%, 100 °C, 1 h; 32%, 100 °C, 12 h).

Mechanistically, transition metal-catalyzed intramolecular cyclocarbonylation of 1,6-diynes, 1,6-enynes, and 1,6-diynes mostly proceeds via metalacycles. In our case, however, it may be reasonable to consider the intermediacy of hydridopalladium species generated from the reaction of palladium(0) with an acid [12]. Here, we propose a hydrido mechanism for the cyclocarbonylation of 1,6-diynes as shown in Scheme 2. The palladium(0) complex undergoes oxidative addition to trifluoromethanesulfonic acid forming a palladium hydride species, which inserts a triple bond in **1a** to give the vinylic complex. An intramolecular ring-formation by the insertion of another triple bond followed by the insertion of carbon monoxide gives the acyl complex. A second intramolecular insertion takes place with the alkene to give the alkylpalladium, which undergoes β-hydride elimination releasing the product **2a**. Since β-hydride elimination occurs in a syn fashion, the product is not cyclopentadienone but bicyclooctadienone. The observed selectivity for the diyne **1e** bearing ethyl and phenyl subustituents on the respective triple bonds indicates that the hydridopalladium adds to the triple bond bearing the ethyl substituent preferentially. In Scheme 3, a presumable mechanism for the formation of butenolide **5** from 1,5-diyne **4** has been depicted. Under an increased pressure, insertion of carbon monoxide into the palladium–carbon bond may take place to give an acyl species **6** rather than



Scheme 2. Proposed mechanism for the formation of **2a** from **1a**.



Scheme 3. Presumable mechanism for the formation of **5** from **4**.

the intramolecular acetylene insertion. Consecutive insertion of another triple bond (acylpalladation) and carbon monoxide followed by lactonization via the enol form should give rise to the observed butenolide **5**. The present reaction proceeds via acylpalladation of alkyne that has been rarely realized [15].

In summary, palladium complexes could be employed as catalyst for the intramolecular [2+2+1] cyclocarbonylation of 1,6-diynes to present a new route to the formation of alkylidenecyclopentenones. Under an increased pressure the reaction of 1,6- and 1,5-diynes took place in a different fashion via the tandem insertion of carbon monoxide to afford alkylidenebutenolides.

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