

Dicobalt Octacarbonyl-Catalyzed Tandem Cycloaddition Reaction between Diyne and Diene under CO

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Treatment of 1,7-diphenyl-1,6-heptadiyne and a symmetric butadiene such as 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene with $\text{Co}_2(\text{CO})_8$ (5 mol %) in CH_2Cl_2 at 110 °C under 30 atm CO for 18 h afforded a 5.5.6 tricyclic enone in high yields. For unsymmetrical dienes such as 2-methyl-1,3-butadiene, 2-methyl-1,3-pentadiene, and 3-methyl-1,3-pentadiene, two separable regioisomers were obtained. The catalytic reactions described are experimentally quite simple and provide a very useful synthetic procedure for the syntheses of [5.5.6] tricyclic enones.

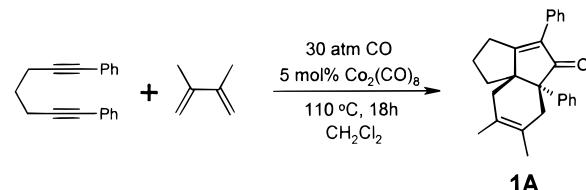
Introduction

Recently, cyclopentadienones have attracted much attention due to their high potential for synthesis.¹ However, due to their strong tendency to dimerize, they have limited use in organic synthesis. Recently, the generation and stabilization of cyclopentadienones through the employment of transition metals has become popular and attractive.² However, until the publication of our recent investigations³ the application of the transition metal mediated reaction to organic synthesis has been hampered by the necessity for the presence of specific substituents and a demetalation step.⁴ There have been many studies⁵ on the [2 + 2 + 2] cycloaddition reaction of a diyne with an alkyne or alkene but no successful examples of the catalytic tandem [2 + 2 + 1] and [4 + 2]

cycloaddition reaction of diyne with diene under CO have been reported. Herein, we report the construction of novel tricyclic compounds through the dicobalt octacarbonyl-catalyzed tandem [2 + 2 + 1] and [4 + 2] cycloaddition reaction between diyne and diene under CO pressure.

Results and Discussion

Treatment of 1,7-diphenyl-1,6-heptadiyne **1** and 2,3-dimethyl-1,3-butadiene with $\text{Co}_2(\text{CO})_8$ (5 mol %) in CH_2Cl_2 at 110 °C under 30 atm of CO for 18 h afforded 5.5.6 tricyclic enone **1A** in 80% yield without any noticeable amounts of byproducts (eq 1).



No isomerization was observed. An X-ray diffraction study of **1A** confirmed the structure (see the Supporting Information). Compound **1A** was the tandem [2 + 2 + 1]/[4 + 2] cycloaddition reaction product. The scope of the catalytic tandem cycloaddition reaction was examined for the reaction of **1** with various dienes (Table 1). For the unsymmetrical dienes such as 2-methyl-1,3-butadiene, 2-methyl-1,3-pentadiene, and 3-methyl-1,3-pentadiene, two regioisomers **A** and **B**, which were easily separated by column chromatography, were obtained in various ratios depending upon the diene. The regioisomer **A** was slightly more favorable than **B** presumably due to the less steric congestion. The **A:B** ratio was 2.5:1 for

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Table 1. Tandem [2 + 2 + 2]/[4 + 2] Cycloaddition Reactions^a

entry	diene	product	yield(%) ^b
1			80
2		2A	91 (65:26)
2		2B	
3		3A	78 (45:33)
3		3B	
4		4A	71 (52:19)
4		4B	
5			27
6			87

^a Reaction conditions: 1,7-diphenyl-1,6-heptadiyne (1.22 mmol), 5 mol % Co₂(CO)₈, CH₂Cl₂, 110 °C, 18 h. ^b Isolated yield.

2-methyl-1,3-butadiene, 1.4:1 for 2-methyl-1,3-pentadiene, and 2.7:1 for 3-methyl-1,3-pentadiene. The molecular structure of **4A** was also confirmed by an X-ray diffraction study (see the Supporting Information). When 1-methoxy-2,4-hexadiene was used, the expected product was not obtained. Instead, **5C** was isolated in 27% yield with the recovery of reactant in 65% yield. Compound **5C** might be derived from an electrophilic attack on cyclopentadienone followed by a double bond migration. Subjecting 1,3-cyclohexadiene to the same reaction conditions provided the expected tetracyclic enone **6A** in 87% yield.

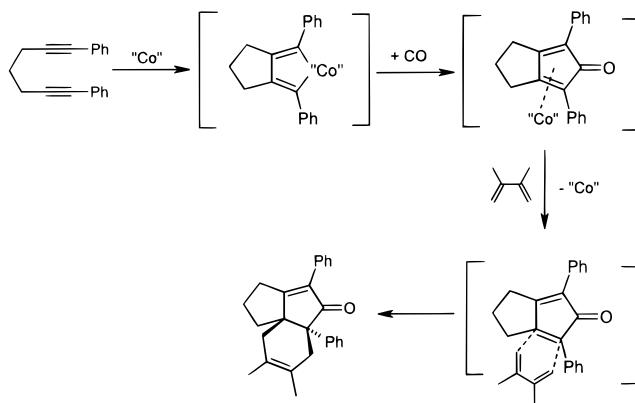
The generality of the cobalt carbonyl-catalyzed tandem cycloaddition was also tested with several diynes (Table 2). The tandem cycloaddition of diynes **7–9** having a tertiary center at the 4-position with diene under CO gave **7A–9A** in 78, 90, and 84% yields, respectively. For an oxygen-bridged diyne **10** with two phenyl groups at the terminals, the oxatricyclic enone derivative **10A** was obtained in 74% yield. However, when a terminal diyne **11** having a quaternary center at the 4-position was subjected to catalyzed coupling with diene, **11D** was isolated in 92% yield. Compound **11D** was the major product when the reaction was carried out in the absence of diene.^{3c}

We have screened other diynes such as 1,7-disubstituted 1,6-heptadiyne **12** (R = TMS, TBDS, *t*-Bu) and 1,8-diphenyl-1,7-octadiyne. However, no reaction was observed. It seems that the existence of phenyl groups at the external termini of the diyne substrate is an important factor for the tandem cycloaddition to proceed. A substrate (**13**) having one carbon longer in the

Table 2. Tandem [2 + 2 + 2]/[4 + 2] Cycloaddition Reactions with Various Diynes^a

entry	diyne	product	yield(%)
1			78
2			90
3			74
4			84
5			92
6			N.R.
7			N.R.

^a Reaction conditions: diyne (1.22 mmol), 5 mol % Co₂(CO)₈, CH₂Cl₂, 110 °C, 18 h. ^b Isolated yield.

Scheme 1

tether did not afford the corresponding tricyclic compounds. Thus, the dicobalt octacarbonyl-catalyzed tandem [2 + 2 + 1] and [4 + 2] cycloaddition of diyne with diene is quite unique to 1,7-diphenyl-1,6-heptadiynes. A plausible reaction mechanism was provided in Scheme 1.

We have demonstrated that by the judicious choice of diyne and diene, a catalytic tandem [2 + 2 + 1] and [4 + 2] cycloaddition reaction can be carried out to yield a novel [5.5.6] tricyclic enone system. The experimental

simplicity and the high conversion rate of the cycloaddition reaction are noteworthy. Further studies on the application of the reaction are in progress.

Experimental Section

General Methods. Unless otherwise noted, starting materials were obtained from commercial suppliers and used as received. ^1H NMR spectra were recorded on spectrometers operating at 300 MHz in CDCl_3 . Coupling constants (J) are reported in Hz. Chromatography refers to flash chromatography on E. Merck silica gel 60, 40–60 μm .

Cobalt-Catalyzed Tandem [2 + 2 + 1] and [2 + 2 + 2] Cycloaddition.

Compounds **1** (0.33 g, 1.22 mmol), $\text{Co}_2(\text{CO})_8$ (21 mg, 0.061 mmol), and 15 mL of CH_2Cl_2 were put in a 100 mL stain steel reactor. CO was slowly flowed for 2 min, and 2,3-dimethyl-1,3-butadiene (0.28 mL, 2.44 mmol) was added to the reactor. The reactor was pressured by 30 atm of CO at room temperature and heated at 110 °C for 18 h. After the reactor was cooled to room temperature, the excess CO gas was relieved and the solvent was evaporated to dryness. The residue was chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v, 20:1). Removal of the solvent gave **1A** in 80% (0.35 g). **1A**: ^1H NMR (CDCl_3) δ 7.59 (d, 7.2 Hz, 2 H), 7.39 (t, 7.2 Hz, 2 H), 7.31–7.12 (m, 4 H) 7.07 (d, 7.2 Hz, 2 H), 2.88 (ddd, 19.0, 11.0, 3.1 Hz, 1 H), 2.65 (d, 14.0 Hz, 1 H), 2.57 (d, 14.0, 1 H), 2.63–2.54 (m, 1 H), 2.30 (d, 14.0 Hz, 1 H), 2.20 (d, 14.0 Hz, 1 H), 2.15 (m, 1 H), 1.77 (m, 1 H), 1.62 (s, 3 H), 1.56 (s, 3 H), 1.40 (dd, 7.5, 5.2 Hz, 1 H), 0.85 (m, 1 H) ppm; ^{13}C NMR (CDCl_3) δ 210.9, 184.6, 143.1, 135.0, 131.7, 129.7, 128.6, 128.4, 128.1, 127.8, 127.3, 126.3, 125.7, 65.9, 62.9, 60.3, 41.0, 39.3, 33.9, 25.7, 23.3, 19.4, 19.0, 15.3 ppm; $\nu(\text{CO})$ 1687 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}$: C, 88.09; H, 7.39. Found: C, 88.14; H, 7.59.

Characterization of other new compounds was given in the Supporting Information.

Crystal Structure Determination of **1A and **4A**.** Crystals of **1A** and **4A** were grown by slow diffusion of hexane to diethyl ether solution and slow evaporation of the resulting solution in a freezer. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer with a $\omega/2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are in listed in S1–S10 (see the Supporting Information). The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares methods with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

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Supporting Information Available: Tables of the crystal data, bond lengths and angles, atomic coordinates, anisotropic thermal parameters of **1A** and **4A**, the ORTEP drawings of **1A** and **4A**, and characterization of new compounds **2A**, **2B**, **3A**, **3B**, **4A**, **4B**, **5C**, **6A**, **7**, **7A**, **8**, **8A**, **9**, **9A**, and **10A**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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