

## Reductive Pauson–Khand reaction using the (RC≡CR')Co<sub>2</sub>(CO)<sub>6</sub>/CF<sub>3</sub>COOH system

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### Abstract

Cyclopentanones are formed in the Pauson–Khand reaction of cobalt alkyne complexes in the presence of TFA. The in situ precursor complexes were formed on the reduction of CoBr<sub>2</sub> by zinc metal in the presence of the alkynes under carbon monoxide atmosphere.

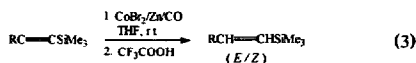
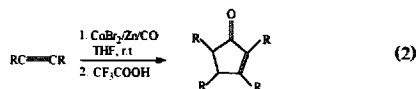
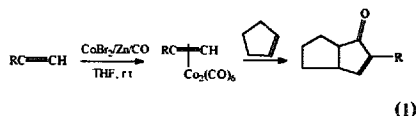
**Keywords:** Cobalt; Carbon monoxide; Alkyne; Carbonylation; Reduction; Cyclopentanones

### 1. Introduction

Pauson–Khand cyclopentenone synthesis using (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> complexes has widespread applicability due to its operational simplicity [1,2]. This reaction is still under active investigation, and several recent modifications have been reported [3,4]. Reductive Pauson–Khand cyclizations have been reported by Serratosa and coworkers [5], and later studied by Pauson and coworker [6] using Smit–Caple dry state adsorption conditions which involve adsorbing the alkyne complex on silica with warming in air at 70 °C. Formation of cyclopentanones has been reported in the cyclization of a series of N-protected allyl propargyl amines, to give saturated azabicyclo [3.3.0.] octanones in the absence of oxygen under these conditions [7]. An irradiation technique has also been reported to be efficient for the reductive Pauson–Khand reaction in the absence of oxygen [6]. The formation of the cyclopentanones along with cyclopentenones has also been reported by Pauson and coworkers [8] in polar solvents such as DMSO and CH<sub>3</sub>CN/CHCl<sub>3</sub> solvent systems.

In recent years, we have shown that the (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> complex prepared from the reduction of CoBr<sub>2</sub> with Zn in the presence of carbon monoxide atmosphere and alkyne is useful in the Pauson–Khand

reaction (Eq. (1)) [9]. We have also reported the formation of cyclopentanones and alkenylsilanes from the corresponding cobalt carbonyl complexes of alkynes with TFA (Eqs. (2) and (3)) [10].



We wish to report that the reaction of the (alkyne)Co<sub>2</sub>(CO)<sub>6</sub>–CF<sub>3</sub>COOH reagent system with norbornene gives the corresponding reductive Pauson–Khand cyclopentanone.

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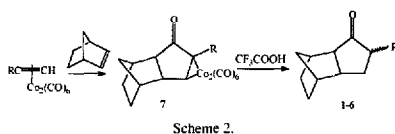
## 2. Results and discussion

We have observed that the reaction of the cobalt carbonyl complex of 1-dodecyne with norbornene in the presence of TFA results in the formation of a reductive Pauson–Khand product, the cyclopentanone (**1**) in 60% yield. The generality of this transformation has been further studied with a number of alternate alkynes, and the results are summarised in Scheme 1.

In all cases, the corresponding Pauson–Khand products are also formed in minor amounts. The cyclopentanones were not formed previously in the reaction of (alkyne) $\text{Co}_2(\text{CO})_6$  complexes with norbornene in the absence of TFA [9]. The formation of cyclopentanones is of interest, since such reduced products have been reported only in the case of intramolecular Pauson–Khand reaction under Smit–Cuple adsorption conditions [5–8].

It is also of interest to note that the reaction of the  $(\text{PhC}\equiv\text{CH})\text{Co}_2(\text{CO})_6$  complex with norbornene and TFA produces the corresponding cyclopentanone as a single epimer. Presumably, the phenyl substituent would be placed in the *exo* face of the bicyclooctyl moiety as it is expected to be stable under these conditions [11]. In the case of alkyl substituted alkynes, inseparable *exo/endo* mixtures of cyclopentanones are obtained. This is not entirely unexpected, as the steric requirements of the bulky substituents are expected to be less pronounced [11].

The mechanism for the formation of a reductive Pauson–Khand product under the silica gel adsorption conditions mentioned earlier is not clear [6]. It was speculated that the solvent used is the likely source of hydrogen [6]. When the TFA was added to a pre-heated mixture of  $(\text{PhC}\equiv\text{CH})\text{Co}_2(\text{CO})_6$  complex and norbornene at 60–70°C for 1 h, only the corresponding Pauson–Khand cyclopentenone was formed. A similar result was also observed in the reaction of (1-heptyne) $\text{Co}_2(\text{CO})_6$  complex and norbornene with TFA. Clearly, the addition of TFA to the reaction mixture before heating is necessary for the formation of cyclopentanones. Probably, the TFA needs to be present to



react with the intermediate **7** to give the cyclopentanones (**1–6**, Scheme 2).

Alternatively, the TFA might first give the  $\text{HCo}(\text{CO})_3$  species [12], which could convert the complexed cyclopentanone to the reduced product (Scheme 2). This tentative mechanism may help in rationalizing the results.

Attempts to minimise the formation of Pauson–Khand cyclopentanones as side products by changing the order of addition of norbornene and TFA were not successful. We have observed that the reaction of  $(\text{PhC}\equiv\text{CSiMe}_3)\text{Co}_2(\text{CO})_6$  with norbornene and TFA gave only the corresponding *E* and *Z* mixture of alkenylsilane in 40% yield, along with small amounts of unidentified carbonyl products. The *E/Z* isomeric ratio 2:1 found is similar to that observed earlier in the absence of norbornene [10]. This result indicates that the rate of reaction of this complex with TFA is faster than the reaction with norbornene. The reaction with norbornadiene also failed to give the reduced Pauson–Khand product in the present reaction conditions. Only the corresponding Pauson–Khand cyclopentenone was obtained.

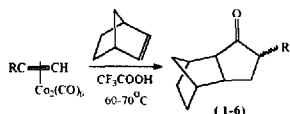
The reaction of the cobalt carbonyl complex of diphenylacetylene with norbornene and TFA is not clean. In this case, only the Pauson–Khand cyclopentanone was obtained. The change in reactivity with different substrates had also been reported under solid state adsorption conditions. Notably, internal alkynes failed to give cyclopentanones under these conditions [6].

Although the mechanistic details are not conclusive at this stage, the present observations should be helpful for further mechanistic and synthetic studies.

## 3. Experimental details

### 3.1. General

All reactions were carried out under dry nitrogen atmosphere. The THF was freshly distilled over sodium–benzophenone ketyl. 1-alkynes and diphenylacetylene were prepared following a literature procedure [13]. Norbornene and alkenes supplied by Fluka, Switzerland were used for the reactions. Activated zinc dust was prepared by treating commercial Zn dust with 1%  $\text{H}_2\text{SO}_4$ , washing with water, acetone and drying at 150°C for 4 h under vacuum. Anhydrous  $\text{CoBr}_2$  was



1. R = n-C<sub>10</sub>H<sub>21</sub>, 60%
2. R = n-C<sub>8</sub>H<sub>17</sub>, 60%
3. R = n-C<sub>6</sub>H<sub>13</sub>, 56%
4. R = n-C<sub>5</sub>H<sub>11</sub>, 58%
5. R = n-C<sub>4</sub>H<sub>9</sub>, 55%
6. R = Ph, 40%

Scheme 1.

prepared from the hydrated complex. It was kept in an air oven at 150°C for 5–6 h, further dried at 150°C for 4 h under vacuum and was kept under nitrogen in a desiccator. Carbon monoxide was generated by dropwise addition of formic acid (98%) to conc. H<sub>2</sub>SO<sub>4</sub> at 90°C using an apparatus recommended for utilization in the carbonylation of organoboranes [14]. IR spectra were recorded on a Jasco FT-5300 with polystyrene as reference. The <sup>13</sup>C NMR spectra were recorded on a Bruker AC-200 spectrometer with CDCl<sub>3</sub> as solvent and TMS as reference. Column chromatography was carried out on silica gel (100–200 mesh) using hexane/ethyl acetate as eluent.

### 3.2. Representative procedure for the reaction of (n-C<sub>10</sub>H<sub>21</sub>C≡CH)Co<sub>2</sub>(CO)<sub>6</sub> complex with CF<sub>3</sub>COOH in the presence of norbornene

The (n-C<sub>10</sub>H<sub>21</sub>C≡CH)Co<sub>2</sub>(CO)<sub>6</sub> (5 mmol) was prepared by reducing CoBr<sub>2</sub> (2.18 g, 10 mmol) with Zn (0.71 g, 11 mmol) and n-C<sub>10</sub>H<sub>21</sub>C≡CH (0.88 g, 5 mmol) in THF (60 ml) and stirring for 3 h while bubbling CO at 25°C. Norbornene (0.94 g, 10 mmol) and trifluoroacetic acid in excess (3 ml) were added, and the contents were stirred at 60–70°C for 16 h. The cobalt carbonyl species completely decomposed during this time. The contents were brought to room temperature and the organic layer was extracted with ether (30 ml) after dilution with water (10 ml). The organic layer thus obtained was washed successively with water (20 ml), 10% NaHCO<sub>3</sub> solution, dried over anhydrous MgSO<sub>4</sub> and concentrated. The crude product was subjected to column chromatography on silica gel. The corresponding cyclopentanone was isolated in 60% (0.87 g) yield with 1–2% ethyl acetate in hexane as eluent. The product was identified by IR, <sup>13</sup>C NMR and by mass spectral data.

This procedure was followed for other (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> complexes, and the results are summarised in Scheme 1.

#### 3.2.1. Compound 1

IR  $\nu$ (CO): 1734 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.7–1.07 (m, 8H), 1.11–1.18 (m, 13H), 1.41–1.60 (b, 3H), 1.7–1.90 (b, 2H), 2.01–2.48 (m, 8H). <sup>13</sup>C NMR:  $\delta$  13.9, 22.6, 27.2, 27.5, 28.0, 28.1, 28.4, 29.2, 29.4, 29.5, 29.6, 31.8, 32.3, 32.4, 32.8, 34.0, 39.1, 40.3, 40.7, 41.7, 42.6, 43.3, 48.8, 49.5, 55.1, 55.3, 220.6, 223.5. Mass (*m/z*): 290 (M<sup>+</sup>, 20%), 163 (30%), 150 (80%), 95 (30%), 83 (100%), 66 (40%), 55 (30%), 41 (40%).

#### 3.2.2. Compound 2

Yield 60% (0.70 g). IR  $\nu$ (CO): 1735 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.81–0.84 (m, 3H), 1.07–1.19 (m, 14H), 1.43–1.50 (b, 3H), 1.65–1.90 (b, 2H), 2.25–2.54 (m, 8H). <sup>13</sup>C

NMR:  $\delta$  14.0, 22.6, 27.3, 27.5, 28.2, 28.4, 29.2, 29.4, 29.7, 31.8, 32.3, 32.8, 34.1, 34.2, 39.2, 40.3, 40.8, 41.7, 42.6, 43.4, 48.9, 49.6, 55.2, 55.4, 220.9, 223.8. Mass (*m/z*): 262 (M<sup>+</sup>, 30%), 178 (50%), 163 (30%), 150 (80%), 93 (50%), 83 (100%), 67 (60%), 55 (50%), 41 (70%).

#### 3.2.3. Compound 3

Yield 56% (0.65 g). IR  $\nu$ (CO): 1734 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.82–0.85 (m, 3H), 1.0–1.3 (m, 10H), 1.40–1.49 (b, 5H), 1.68–1.90 (b, 2H), 2.18–2.58 (m, 6H). <sup>13</sup>C NMR:  $\delta$  13.9, 22.5, 27.2, 27.4, 27.7, 28.0, 28.1, 28.3, 28.4, 29.1, 29.3, 31.6, 32.2, 32.4, 32.7, 34.1, 34.2, 39.1, 40.3, 40.7, 41.6, 42.6, 43.3, 48.8, 49.6, 55.1, 55.3, 220.9, 223.9. Mass (*m/z*): 234 (M<sup>+</sup>, 30%), 163 (40%), 150 (70%), 93 (30%), 83 (100%), 67 (60%), 55 (50%), 41 (75%).

#### 3.2.4. Compound 4

Yield 58% (0.64 g). IR  $\nu$ (CO): 1734 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.8–0.9 (m, 3H), 1.07–1.28 (m, 8H), 1.46–1.54 (b, 5H), 1.72–1.77 (b, 2H), 2.31–2.60 (m, 6H). <sup>13</sup>C NMR:  $\delta$  13.9, 22.4, 26.9, 27.1, 28.0, 28.1, 28.4, 28.7, 31.6, 31.8, 32.2, 32.6, 32.7, 34.1, 34.2, 36.0, 39.1, 40.3, 40.7, 41.7, 42.6, 43.3, 48.8, 49.6, 55.1, 55.3, 221.1, 224.1. Mass (*m/z*): 220 (M<sup>+</sup>, 10%), 178 (40%), 150 (55%), 93 (55%), 83 (65%), 67 (80%), 55 (60%), 41 (100%).

#### 3.2.5. Compound 5

Yield 55% (0.57 g). IR  $\nu$ (CO): 1734 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.79–0.86 (m, 3H), 1.0–1.27 (m, 6H), 1.39–1.50 (b, 5H), 1.67–1.88 (b, 2H), 2.17–2.56 (m, 6H). <sup>13</sup>C NMR: 13.9, 22.6, 22.8, 28.2, 28.3, 28.4, 28.5, 29.4, 29.5, 29.8, 30.2, 32.1, 32.6, 32.9, 34.2, 34.3, 36.2, 39.2, 40.4, 40.8, 41.8, 42.7, 43.5, 48.9, 49.6, 55.2, 55.4, 220.8, 223.7. Mass (*m/z*): 206 (M<sup>+</sup>, 20%), 178 (25%), 150 (50%), 95 (38%), 83 (90%), 66 (100%), 55 (40%), 41 (100%).

#### 3.2.6. Compound 6

Yield 40% (0.45 g). IR  $\nu$ (CO): 1732 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  1.15–1.19 (m, 4H), 1.23–1.56 (m, 4H), 2.19–2.28 (m, 3H), 2.55–2.65 (m, 2H), 7.0–7.32 (m, 5H). <sup>13</sup>C NMR:  $\delta$  28.0, 28.1, 34.3, 34.6, 39.2, 40.4, 42.5, 54.8, 55.2, 126.7, 127.9, 128.3, 128.4, 137.9, 217.6. Mass (*m/z*): 226 (M<sup>+</sup>, 60%), 163 (25%), 129 (25%), 115 (30%), 104 (100%), 91 (40%), 77 (60%), 66 (50%), 39 (40%).

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