

## Bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne Complexes Mediated [2 + 2 + 1] Cycloaddition: the Formation of 3-Substituted Cyclopentenone Derivatives

Chisato Mukai, Masahiko Uchiyama and Miyoji Hanaoka\*

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan.

On heating, bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes undergo a [2 + 2 + 1] cycloaddition with norbornadiene or norbornene to afford the corresponding 3-substituted cyclopentenone derivatives, which could hardly be obtained in the cobalt-complexed alkyne-mediated Pauson–Khand reaction.

The Pauson–Khand reaction<sup>1</sup> is a formal [2 + 2 + 1] cycloaddition of alkynes, alkenes and carbon monoxide through hexacarbonyldicobalt-alkyne complexes **1**. This useful cyclopentenone formation reaction has been successfully applied to the synthesis of various natural products.<sup>2</sup>

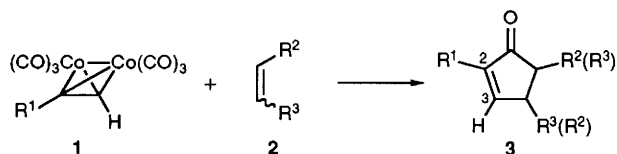
In an intermolecular Pauson–Khand reaction,<sup>1</sup> the substituted terminals of the cobalt-complexed alkynes **1** are exclusively incorporated at the C-2 position of the resulting cyclopentenone derivatives **3**. However, no report<sup>†</sup> dealing with the extension of the method to the formation of 3-substituted cyclopentenone derivatives in a Pauson–Khand type reaction has so far been made. We describe a novel method for production of the 3-substituted cyclopentenone derivatives mediated by molybdenum-alkyne complexes.

Bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes **4**, isoelectronic compounds of hexacarbonyldicobalt congeners **6**, were prepared according to the literature.<sup>3</sup> The molybdenum-alkyne complex **4a** was heated under reflux with norbornadiene **7** in toluene under a nitrogen atmosphere for 6 h to give, after chromatographic separation, the 2-phenylcyclopentenone derivative **9a** and the 3-phenyl derivative **10a** in 45 and 32% yields, respectively. The former was identified with an authentic sample<sup>4</sup> obtained from the reaction of **6** with norbornadiene. The 3-phenyl derivative **10a** showed a diagnostically higher field shifted vinylic proton at  $\delta$

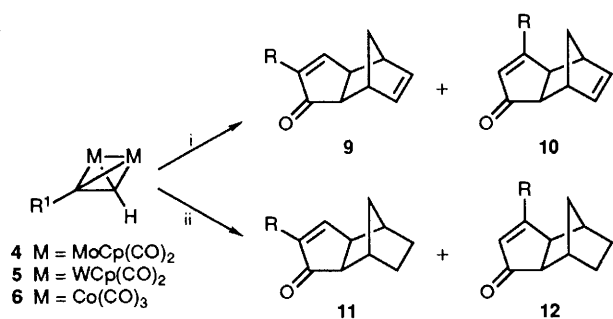
6.61 in its <sup>1</sup>H NMR spectrum.<sup>‡</sup> The *endo*-structure for **10a** could be easily ruled out by comparing its spectroscopic data with those of the corresponding *endo*-adduct<sup>5</sup> in the literature. *p*-Methylphenyl and *n*-butyl derivatives **4b** and **c** also afforded the 'abnormal' 3-substituted adducts **10b** and **c** along with the 'normal' Pauson–Khand products **9b** and **c**.§ However, the molybdenum complexed trimethylsilylacetylene **4d** produced only 'normal' Pauson–Khand product **9d**§ in 39% yield. The results are summarised in Table 1.

When an isoelectronic tungsten complex **5a**<sup>6</sup> was submitted to the [2 + 2 + 1] cycloaddition reaction with norbornadiene, cycloadducts **9a** and **10a** were obtained, but the ratio of **10a** to **9a** was significantly decreased. Although the desired 3-substituted cyclopentenones **12** were consistently formed in the reaction of **4** with norbornene **8**, the yields were rather lower compared with the case of norbornadiene.

The molybdenum-alkyne complex was found to be effective for intramolecular cyclisation as well. The complex **13** prepared from diethyl allylpropynylmalonate was heated under reflux in toluene for 8 h under nitrogen to give the bicyclo[3.3.0]octene derivative **14** in 50% yield.

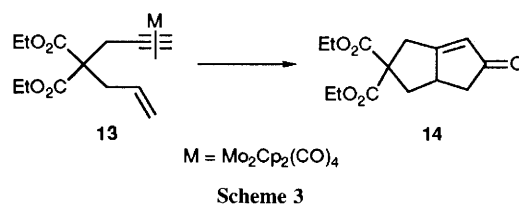


Scheme 1 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = alkyl, aryl, TMS, alkylthio etc.



a R = Ph, b R = *p*-Me-C<sub>6</sub>H<sub>4</sub>, c R = Bu, d R = SiMe<sub>3</sub>

Scheme 2 Reagents: i, norbornadiene **7**; ii, norbornene **8**



Scheme 3

Table 1 [2 + 2 + 1] Cycloaddition of metal-complexed alkynes with alkenes

Complexed alkyne	Cycloadduct (%)	
	2-Substituted	3-Substituted
<b>4a<sup>a,c</sup></b>	<b>9a</b> (45)	<b>10a</b> (32)
<b>4b<sup>a,c</sup></b>	<b>9b</b> (31)	<b>10b</b> (25)
<b>4c<sup>a,c</sup></b>	<b>9c</b> (28)	<b>10c</b> (20)
<b>4d<sup>a,c</sup></b>	<b>9d</b> (39)	—
<b>5a<sup>b,c</sup></b>	<b>9a</b> (33)	<b>10a</b> (3)
<b>4a<sup>b,d</sup></b>	<b>11a</b> (5)	<b>12a</b> (3)
<b>4c<sup>b,d</sup></b>	<b>11c</b> (18)	<b>12c</b> (11)

<sup>a</sup> Refluxed in toluene. <sup>b</sup> Heated in toluene at 160 °C in a sealed tube. <sup>c</sup> With norbornadiene. <sup>d</sup> With norbornene.

‡ The vinylic proton of the 2-phenyl derivative **9a** appeared at  $\delta$  7.69 in its <sup>1</sup>H NMR spectrum which was shifted 1.08 ppm downfield from the vinylic proton of **10a**. This observation corroborates the 3-phenyl substituted structure for **10a**.

§ The 2-substituted cyclopentenone derivatives were identified with the authentic specimen prepared by using the cobalt-complexed alkynes. In all cobalt-complexed alkyne mediated experiments we examined, no 3-substituted products could be detected by thin-layer chromatography.

† Krafft<sup>7</sup> has recently isolated and characterised 3-methyl-[2-(phenylthio)ethyl]-2-cyclopentenone in 2–3% yield along with the 2-methyl congener (65%) in the reaction of the cobalt-complexed propyne with homoallylphenylsulfide. Pauson<sup>1c</sup> also reported the formation of trace amounts of the 3-substituted cyclopentenone derivatives without any characterisation of their structures.

In summary, we describe the first practical example† of the formation of an 'abnormal' 3-substituted cyclopentenone derivative in a Pauson–Khand type reaction using bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes **4**, although their reactivity and regioselectivity are not satisfactory yet. Further studies on optimising the reaction conditions for exclusive production of the 3-substituted cyclopentenones as well as improvement of the reactivity are now in progress.

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