Synthesis of Polycyclic Compounds by the Reaction of $Co_2(CO)_6$ Complexed 1-[*o*-(1-Alkynyl)phenyl]cyclopropanols

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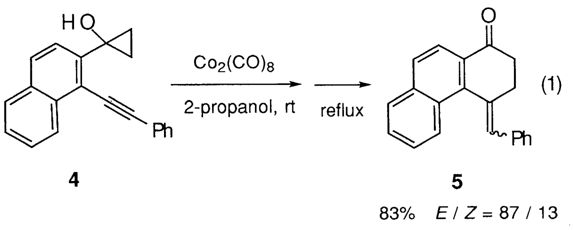
1-[*o*-(1-Alkynyl)phenyl]cyclopropanols are converted to 2,3-dihydro-1-naphthalenone derivatives by heating their hexacarbonyldicobalt complexes in 2-propanol. Furthermore, a new type of isomerization-cyclization reaction proceeds to give 3a,4-dihydro-3*H*-cyclopenta[*a*]inden-2-one derivatives when the same reaction is carried out in the presence of DABCO.

Development of new methods for the construction of carbocycles has been one of the most important issues in the field of synthetic organic chemistry. As an approach toward this goal, we have been studying transition metal promoted reactions of cyclopropanols having an unsaturated moiety based on the assumption that appropriate complexation of transition metal to the unsaturated moiety would enable effective activation of the neighboring cyclopropane ring, resulting in new modes of carbocycle formation.[1-3]

We have already reported that various substituted 2-cyclopentenones are obtained by the rearrangement of 1-(1-alkynyl)cyclopropanols via their hexacarbonyldicobalt ($Co_2(CO)_6$) complexes.[1] In this reaction, it is assumed that alkyne-$Co_2(CO)_6$ moiety, directly connected to the cyclopropane ring, activates the ring effectively leading to the cleavage and recombination of carbon-carbon bond of the cyclopropane. Then we have got an interest in the possibility of constructing polycyclic compounds by using substrates in which alkyne and cyclopropane ring are connected through a benzene ring.

In this paper are described two new types of carbocycle formations using 1-[*o*-(1-alkynyl)phenyl]cyclopropanols via their $Co_2(CO)_6$ complexes.

Treatment of 1-[*o*-(1-alkynyl)phenyl]cyclopropanol **1**[4] with 1.1~1.2 molar amounts of $Co_2(CO)_8$ generated the corresponding **1**-$Co_2(CO)_6$ complex **2** smoothly at rt. Heating this complex in refluxing 2-propanol gave 2,3-dihydro-1-naphthalenone derivative **3** as a mixture of geometric isomers in moderate yield. The results of several substrates are summarized in Table 1. Furthermore, when a naphthyl derivative **4** was employed for this reaction, the 2,3-dihydrophenanthren-1-one derivative **5** was obtained in 83% yield. (Eq. 1) These results indicate that cleavage of carbon-carbon bond of cyclopropanol can be achieved even when phenyl group intervenes between alkynyl group and cyclopropane ring.



83% E/Z = 87 / 13

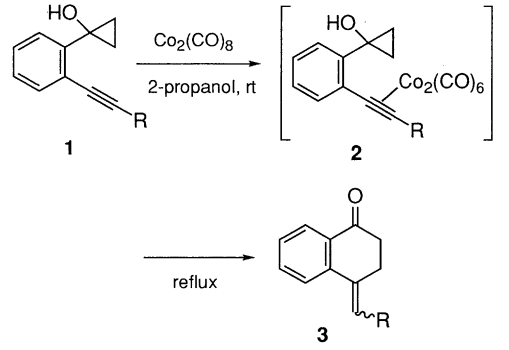
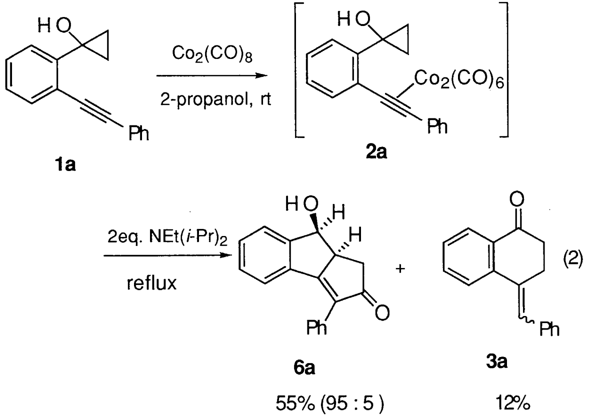


Table 1. Preparation of 2,3-dihydro-1-naphthalenones[a]

R	Reaction Time / h	Yield / %	E/Z
Ph	1	47	60 / 40
Hexyl	3	32	45 / 55
c-Hexyl	0.5	49	70 / 30

[a]In these reactions, cyclopenta[*a*]inden-2-ones **6** are not detected.

During these studies, we happened to find that when the same reaction was carried out in the presence of a tertiary amine, a different kind of product was obtained. Thus, when 1-[*o*-(phenylethynyl)phenyl]cyclopropanol-$Co_2(CO)_6$ complex **2a** was heated in refluxing 2-propanol for 30 min under argon in the presence of 2 molar amounts of ethyldiisopropylamine, a 3a,4-dihydro-3*H*-cyclopenta[*a*]inden-2-one derivative **6a** was produced as a 95:5 diastereomeric mixture in 55% yield with 12% yield of the dihydronaphthalenone **3a**. (Eq. 2) The structure of the major isomer of **6a** was determined by X-ray analysis of the corresponding bromoacetate.



Examination of reaction conditions revealed that the reaction proceeded in better yield at lower temperature (50 °C) and that ethyldiisopropylamine or DABCO gave good yields of **6a**, but use of pyridine gave a trace amount of **6a** and use of DBU did not give **6a** at all.

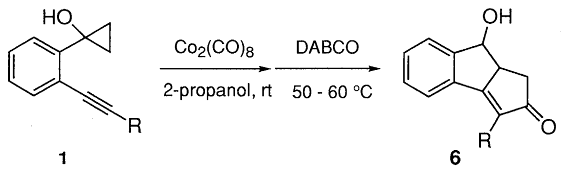


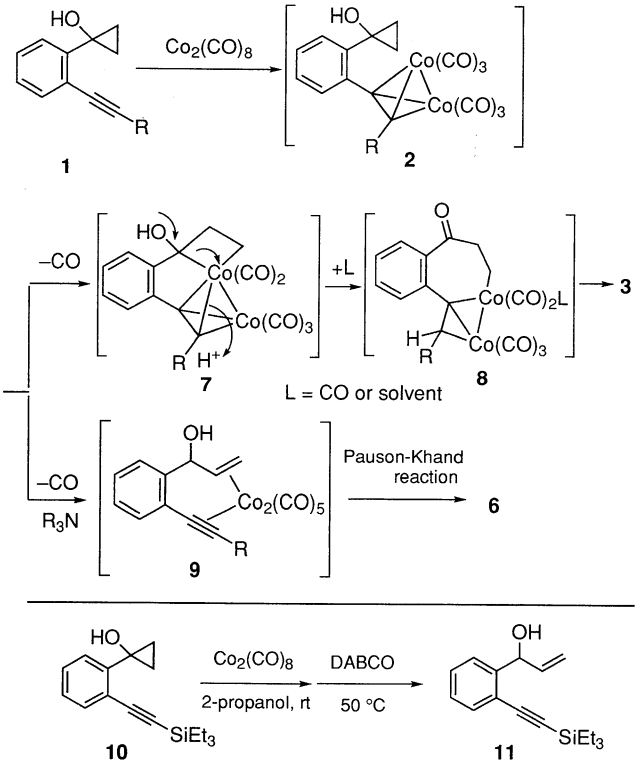
Table 2. Preparation of cyclopenta[*a*]inden-2-ones[a,b]

R	Temperature / °C	Reaction Time / h	Yield / %[c]
Ph	50	1	72
Hexyl	60	3	45
c-Hexyl	60	0.5	60

[a]1 : $Co_2(CO)_8$: DABCO = 1: 1.1 : 6. [b]In these reactions, 2,3-dihydro-1-naphthalenones **3** are detected in less than 10% yield. [c]Obtained as 90:10 to 95:5 mixtures of diastereomers. The major isomers are deduced to have the same relative stereochemistry as shown in **6a** by the analogies of ^1H NMR spectra.

The reactions of several 1-[*o*-(alkynyl)phenyl]cyclopropanol derivatives **1** were examined using 6 molar amounts of DABCO as an additive. As shown in Table 2, not only an aryl-substituted alkynyl derivative but also alkyl-substituted alkynyl derivatives gave the corresponding cyclopenta[*a*]inden-2-one derivatives **6** in moderate to good yield.

Although the exact mechanism of these reactions has not yet been made clear, it is supposed that the reactions proceed as shown in Scheme 1. The reaction in the absence of a tertiary amine proceeds by the oxidative addition of coordinatively unsaturated cobalt species to the neighboring carbon-carbon bond of cyclopropane to give metallacyclic intermediate **7**, which undergoes ring expansion to give **8**. Then reductive elimination gives the 2,3-dihydro-1-naphthalenone derivative **3**. On the other hand, by heating the alkyne-cobalt complex **1** in the presence of a tertiary amine, isomerization of cyclopropanol to allylic alcohol occurs,[5] which is also promoted by the neighboring alkyne-$Co_2(CO)_6$ moiety. Then the produced enyne-cobalt complex **9** undergoes Pauson-Khand reaction[6] to give the product **6**. When a triethylsilyl-substituted derivative **10** was employed for this reaction, an allylic alcohol **11** was isolated albeit in low yield.[7] This fact strongly supports the above proposed mechanism.



Scheme 1.

In conclusion, two new methods for construction of polycyclic carbon skeletons are developed by using $Co_2(CO)_6$ complexed 1-[*o*-(1-alkynyl)phenyl]cyclopropanols. Although the role of the tertiary amine is not obvious, it is noteworthy that two different types of products, that is 2,3-dihydro-1-naphthalenones and 3a,4-dihydro-3*H*-cyclopenta[*a*]inden-2-ones, are obtained depending on the presence or absence of the tertiary amine.

References and Notes

1 N. Iwasawa, *Chem. Lett.*, **1992**, 473; N. Iwasawa and T. Matsuo, *Chem. Lett.*, **1993**, 997; N. Iwasawa and M. Iwamoto, *Chem. Lett.*, **1993**, 1257.

2 N. Iwasawa, Y. Owada, and T. Matsuo, *Chem. Lett.*, **1995**, 115; Y. Owada, T. Matsuo, and N. Iwasawa, *Tetrahedron*, accepted for publication.

3 For related work, see the following examples; M. A. Huffman and L. S. Liebeskind, *J. Am. Chem. Soc.*, **115**, 4895 (1993); I. Ryu, K. Ikura, Y. Tamura, J. Maenaka, A. Ogawa, and N. Sonoda, *Synlett*, **1994**, 941. And references are cited therein.

4 The starting materials **1** were prepared by the reaction of *o*-(1-alkynyl)phenyllithium with iodomagnesium salt of cyclopropanone hemiacetal. See; J. Salaün, F. Bannani, J. Compain, A. Fadel, and J. Ollivier, *J. Org. Chem.*, **45**, 4129 (1980).

5 There are a few examples of transition metal catalyzed isomerization of silyl ethers of cyclopropanols to silyl ethers of allylic alcohols using Rh or Pt complexes. However, the corresponding reaction of unprotected cyclopropanol derivatives has not yet been reported. K. Ikura, I. Ryu, A. Ogawa, N. Kambe, and N. Sonoda, *Tetrahedron Lett.*, **30**, 6887 (1989); K. Ikura, I. Ryu, N. Kambe, and N. Sonoda, *J. Am. Chem. Soc.*, **114**, 1520 (1992). Isomerization of cyclopropyl ethers to allyl ethers catalyzed by ZnI_2 has also been reported by several authors. T. Sugimura, T. Futagawa, A. Mori, I. Ryu, N. Sonoda, and A. Tai, *J. Org. Chem.*, **61**, 6100 (1996) and references are cited therein.

6 N. E. Shore, 'The Pauson-Khand Cycloaddition Reaction for Synthesis of Cyclopentenones' in 'Organic Reactions, Vol. 40,' John Wiley & Sons, Inc., New York (1991), p. 1.

7 The reaction employing this substrate **10** gave a complex mixture of products, from which the allylic alcohol **11** was isolated.