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A Novel Rearrangement of 1-Alkynylcyclopropanol to 2-Cyclopenten-1-one via Dicobalt Hexacarbonyl Complex

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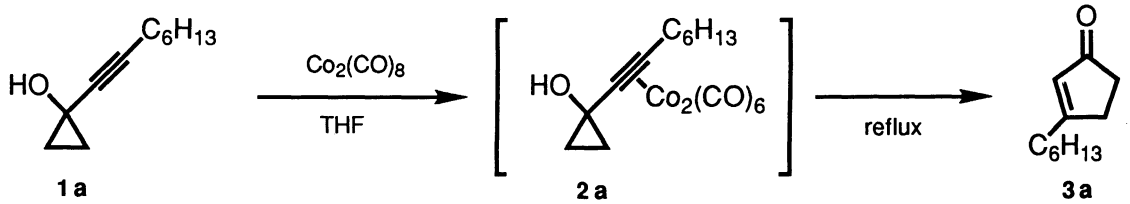
Various 1-alkynylcyclopropanols are found to be converted to 3-substituted 2-cyclopenten-1-ones in good yields by heating their dicobalt hexacarbonyl complexes in refluxing tetrahydrofuran or dimethoxyethane.

Stable alkyne-dicobalt hexacarbonyl complexes are known to be easily prepared from alkynes and dicobalt octacarbonyl and have been widely employed in synthetic organic reactions not only as an alkyne protecting group with a remarkable stabilizing ability of the propargylic cations[1] but also as a component in the Pauson-Khand reaction to give 2-cyclopenten-1-ones by the reaction with olefins.[2]

During the study on the generation of β-keto radicals from cyclopropanol derivatives and their reactions with olefins by the use of manganese(III) 2-pyridinecarboxylate as an oxidant,[3] a novel rearrangement reaction of dicobalt hexacarbonyl-complexed 1-alkynylcyclopropanols to 2-cyclopenten-1-ones was found to proceed under mild reaction conditions. In this paper, preliminary results of these investigations as another utilization of the alkyne-dicobalt hexacarbonyl complexes in organic synthesis will be described.

When 1-octynylcyclopropanol (**1a**) was treated with 1.2 equiv. of dicobalt octacarbonyl in tetrahydrofuran (THF) at room temperature, complete formation of dicobalt hexacarbonyl complex **2a** was observed within a few minutes by thin layer chromatography. The mixture was then refluxed for 8 h under atmospheric pressure under argon, and precipitated inorganic materials were removed by filtration through a small pad of silica gel. Purification of the crude product by preparative thin layer chromatography (silica gel) revealed that 3-hexyl-2-cyclopenten-1-one (**3a**) was produced in 62% yield.[4,5]



1a **2a** **3a**

62% yield

As a novel 1-alkynylcyclopropanol–2-cyclopenten-1-one rearrangement was observed,[6] various reaction conditions were examined next. In the first place, the effect of the solvent on the reaction was examined and the results were summarized in Table 1. As shown in this table, use of the ethereal solvents generally favored the formation of the cyclopentenone **3a**, and by carrying out the reaction in refluxing dimethoxyethane (DME) under diluted conditions, **3a** was obtained in 71% yield. On the contrary, use of the hydrocarbon solvents, which are

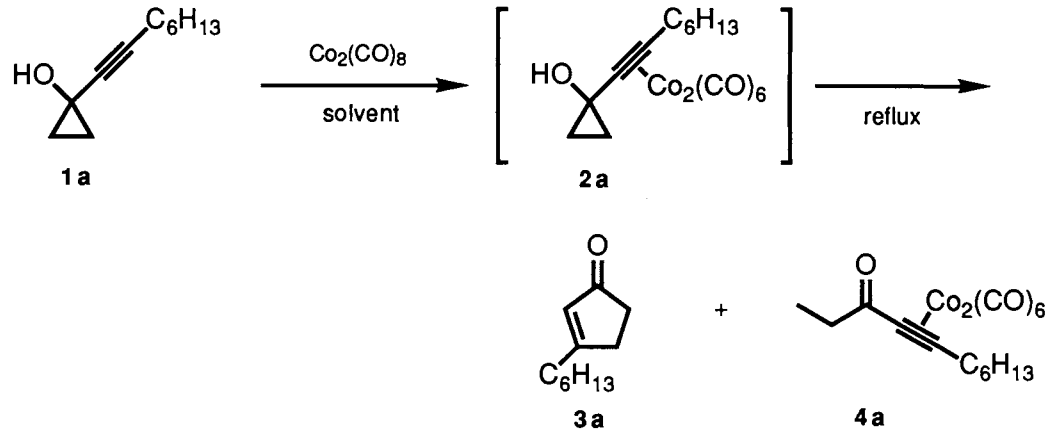


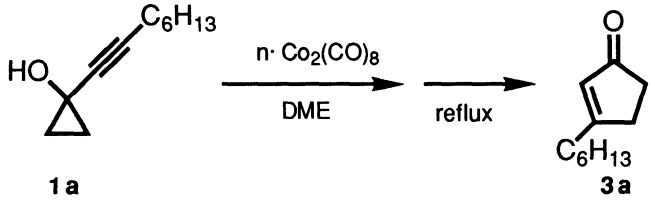
Table 1. Examination of the Solvent

Solvent	Reaction time/h[a)]	Concentration of **1a**/mol·dm^{-3}	Yield/%	
			3a	**4a**
Tetrahydrofuran (THF)	8	0.1	62	0
Dimethoxyethane (DME)	2	0.1	67	0
Dimethoxyethane	2	0.03	71	0
Dioxane	6.5	0.03	45	trace
Hexane	5.5	0.04	13	~70
Benzene	6.5	0.03	40	~40
t-Butanol	2	0.04	27	~30
Carbon tetrachloride [b)]	5.5	0.04	0	0
Ethyl acetate	5	0.03	35	~10

a) In each case, dicobalt hexacarbonyl complex of 1-octynylcyclopropanol (**2a**) disappeared as judged by TLC after the indicated reaction time. b) A complex mixture of unidentified products was obtained in this case.

the solvents of choice in the Pauson-Khand reaction, favored another reaction pathway, that is, the rearrangement of the 1-octynylcyclopropanol-dicobalt hexacarbonyl complex (**2a**) to the ethyl octynyl ketone-dicobalt hexacarbonyl complex (**4a**) proceeded predominantly.[7)] Thus, by carrying out the reaction in refluxing hexane, the complex **4a** was obtained in about 70% yield with the cyclopentenone **3a** in 13% yield. The facile rearrangement of dicobalt hexacarbonyl-complexed 1-alkynylcyclopropanol to dicobalt hexacarbonyl-complexed ethyl alkynyl ketone is noteworthy, because 1-alkynylcyclopropanol is rather stable thermally and, in practice, the starting material was recovered unchanged when 1-octynylcyclopropanol (**1a**) itself was heated in refluxing benzene for 2.5 h.[8)]

Next, we examined the effect of the mole ratio of dicobalt octacarbonyl to 1-alkynylcyclopropanol **1a** on the yield of the cyclopentenone **3a**. As shown in Table 2, use of excess (2 equivalents to **1a**) of dicobalt octacarbonyl had no effect on the yield of **3a**. Furthermore, a catalytic amount of dicobalt octacarbonyl (10-20 mol%) was sufficient to promote the reaction, and **3a** was obtained in moderate yield.



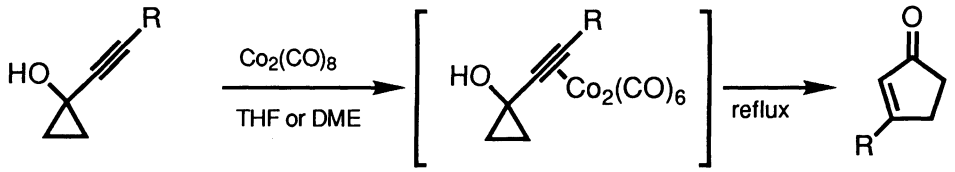
1a **3a**

Table 2. Examination of Mole Ratio of Dicobalt Octacarbonyl

Mole ratio ($Co_2(CO)_8$: **1a**)[a]	Reaction time/h	Yield of **3a**/%
2.0 : 1	1	71
1.1 : 1	2	71
0.2 : 1	2	57
0.1 : 1	2	45

a) Concentration of **1a** is about 0.03 mol·dm^{-3} in each case.

As the reaction was found to proceed efficiently by carrying out the reaction in refluxing THF or DME, the reactions of variously substituted 1-alkynylcyclopropanols were examined using a stoichiometric amount of dicobalt octacarbonyl, and the results were summarized in Table 3. Not only alkyl-substituted alkyne derivatives, but also aryl- or silyl-substituted alkyne derivatives gave the corresponding 3-substituted 2-cyclopenten-1-ones in good to high yields.



1 **3**

Table 3. Reactions of Various 1-Alkynylcyclopropanol[a]

R in **1**	Solvent	Reaction time[b]	Yield of **3**/%[c]
C_6H_{13}	DME	2	71
Ph	DME	2	83
$CH_2OSi^tBuMe_2$	DME	16.5	61
$SiMe_3$	DME	3	77
$SiPh_3$	THF	3	85

a) Mole ratio of $Co_2(CO)_8$ to **1** is about 1.1-1.2:1.0. Concentration of **1** is about 0.03 mol·dm^{-3}.
b) Reaction time indicates approximately the time that the starting cobalt complex of **1** disappeared judged by TLC. c) Satisfactory NMR and IR spectra and elemental analysis and/or high resolution mass spectrum were obtained for each product.

It should be noted that a novel 1-alkynylcyclopropanol–2-cyclopenten-1-one rearrangement is achieved under mild reaction conditions by using the alkyne-dicobalt hexacarbonyl complexes. As 1-alkynylcyclopropanols are easily prepared from cyclopropanone hemiketal and alkynyl Grignard reagents,[9] this reaction would be a useful method for the synthesis of various 3-substituted 2-cyclopenten-1-ones. Further examination of this reaction including the elucidation of the reaction mechanism is now in progress.

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References

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2) 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.
3) N. Iwasawa, S. Hayakawa, K. Isobe, and K. Narasaka, *Chem. Lett.*, **1991**, 1193.
4) The NMR and IR spectra coincided with those of the literature: T. Yoshida and S. Saito, *Chem. Lett.*, **1982**, 165.
5) When 1-octynylcyclopropanol-dicobalt hexacarbonyl complex (**2a**) was isolated by silica gel column chromatography under argon and was heated in refluxing DME, comparable yield of the cyclopentenone **3a** was obtained.
6) To our knowledge, there is no precedent for this type of 1-alkynylcyclopropanol–2-cyclopenten-1-one rearrangement except for one specific example of the pyrolysis of 1-ethynyl-2-methylcyclopropane to 3-methylenecyclopentene. However, this reaction proceeds via thermal [1,5] hydrogen shift of the hydrogen of the methyl substituent. See; V. Dalacker and H. Hopf, *Tetrahedron Lett.*, **1974**, 15.
7) The structure of this complex was confirmed by decomplexation with N-methylmorpholine-N-oxide to give ethyl octynyl ketone, whose NMR and IR spectra supported the structure.
8) 1-Alkylcyclopropanols are known to be easily converted to the corresponding ethyl ketones by acid or base treatment. See; C. H. DePuy, *Acc. Chem. Res.*, **1**, 33 (1968).
9) J. Salaun, F. Bennani, J. C. Compain, A. Fadel, and J. Ollivier, *J. Org. Chem.*, **45**, 4129 (1980).

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