CHEMISTTY LETTERS, pp. 997-1000, 1993.

Rearrangement of 1-Alkynylcyclopropanol to 3-Substituted 2-Cyclopentenone Promoted by a Catalytic Amount of Octacarbonyldicobalt-Triphenylphosphite

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The rearrangement of 1-(1-alkynyl)cyclopropanols is catalyzed efficiently by the combined use of octacarbonyldicobalt and triphenylphosphite to give 3-substituted 2-cyclopentenones in high yields.

In the previous paper,1) we reported that the rearrangement of 1-(1-alkynyl)cyclopropanols to 3-substituted 2-cyclopentenones proceeds by heating their hexacarbonyldicobalt ($Co_2(CO)_6$) complexes in tetrahydrofuran (THF) or dimethoxyethane (DME). In this rearrangement, it was supposed that the reaction would proceed by a catalytic amount of octacarbonyldicobalt ($Co_2(CO)_8$), if the cobalt species liberated from the reaction intermediate could form alkyne-$Co_2(CO)_6$ complex with another molecule of 1-(1-alkynyl)cyclopropanol. In practice, the reaction really proceeded by the use of a 10-20 mol% of $Co_2(CO)_8$, but the efficiency was low and the rearranged product was obtained in moderate yield accompanied by a complex mixture of by-products.1) As this low efficiency could be explained by the instability of the liberated cobalt species,2) it is assumed that the catalytic reaction could be made more efficient by the addition of additives which stabilize the unstable intermediate cobalt species. In this paper, we would like to report the effective promotion of this rearrangement by a catalytic amount of $Co_2(CO)_8$ using triphenylphosphite as the addtive.

In the first place, in order to make clear influences of additives on the reaction, the reaction was examined with a stoichiometric amount of $Co_2(CO)_8$ in the presence of various additives, such as phosphines and phosphites, using 1-(phenylethynyl)cyclopropanol (**1a**) as a substrate. The reaction was carried out as follows: 1-(Phenylethynyl)cyclopropanol (**1a**) was treated with 1.1 mole amounts of $Co_2(CO)_8$ in THF3) at room temperature. After complete formation of **1a**-$Co_2(CO)_6$ complex **2a** was confirmed by thin layer chromatography (TLC), 2 mole amounts of additives were added, and then the mixture was refluxed. Within a few minutes, formation of a new complex **3a**, in which 2 carbonyl ligands were exchanged by 2 molecules of additives,4) was observed and the reaction proceeded from this new complex. When the complex **3a** disappeared as judged by TLC, the reaction was stopped. After filtration of the reaction mixture through a small pad of silica gel, this crude product was purified by preparative TLC. The results were summarized in Table 1.

These results indicate that the reaction also proceeded from the ligands-exchanged complex **3a** with comparable yields to the reaction of the hexacarbonyldicobalt complex **2a**. And as easily seen from the reaction time in the Table I, the reactivity of the ligands-exchanged complex **3a** is controlled mainly by the steric factors of the ligands. Thus, as the bulkier the ligand became, (that is, the larger the cone angle of the ligand became), the faster the reaction proceeded (Entries 2, 3, 4, 5, 7). And the reaction completed in one hour in refluxing THF

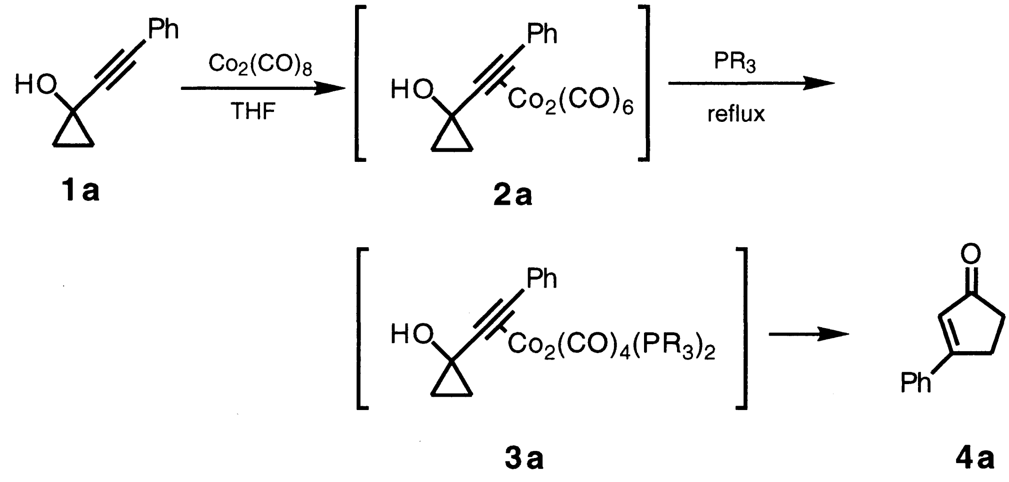


Table 1. Examination of the Additives under the Stoichiometric Conditions

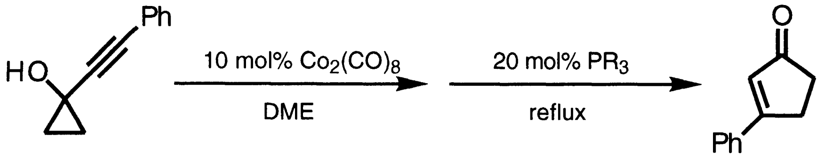
Entry	Additives	Cone angle$^{5)}$	Mole amount	Reaction time/h$^{a)}$	Yield/%
1	none	-	-	6	90
2	PBu^{n}_{3}	130	2	5	71
3	PPh_3	143	2	1	84
4	$P(OMe)_3$	108	2	17$^{b)}$	43
5	$P(OPr^{i})_3$	130	2	11	78
6	$P(OPh)_3$	128	1$^{c)}$	4	70
7	$P(OPh)_3$	128	2	6	86
8	$P(OPh)_3$	128	4$^{d)}$	6$^{b)}$	4

a) In each case, the cobalt complex **3a** disappeared as judged by TLC after the indicated reaction time. b) In these cases, the reactions didn't complete and **3a** was recovered. c) In this case, a complex, in which one carbonyl ligand was exchanged by a phosphite, was formed. d) In this case, the complex **3a** remained in the reaction mixture and no further ligands-exchanged complexes were observed.

by adding PPh_3 as the addtive (Entry 3). The amount of additives also had a great effect on the reaction time, and use of 4 mole amounts of $P(OPh)_3$ retarded the reaction considerably (Entries 6-8).

As the stoichiometric reactions in the presence of phosphines or phosphites proceeded in good yields, we examined the reactions using these additives under catalytic conditions. Thus 10 mol% of octacarbonyldicobalt was added to 1-(phenylethynyl)cyclopropanol (**1a**) in DME, and after the mixture was stirred for 0.5 to 1 h, 20 mol% of the additives were added and the reactions were performed in the same procedure as that of the stoichiometric reactions except that DME was employed as the solvent, and the results were summarized in Table 2.

As shown in this Table, the addition of phosphines or phosphites improved the yields of the rearranged products considerably under the catalytic conditions. In particular, when the reaction was carried out with 10

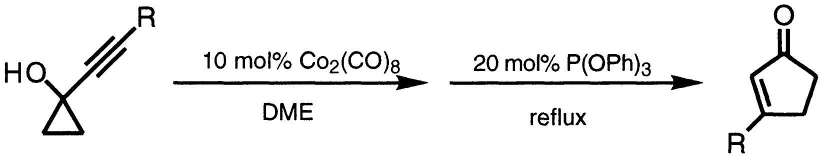


1a **4a**

Table 2. Examination of the Additives in the Catalytic Conditions

PR_3	Reaction time/min[a]	Yield of **4a**/%
none	60	43
PBu^n_3	30	59
PPh_3	20	79
$P(OMe)_3$	60	70
$P(OPr^i)_3$	60	74
$P(OPh)_3$	60	91
$P(OPh)_3$[b]	420	76[c]

a) In each case, 1-(phenylethynyl)cyclopropanol (**1a**) disappeared after the indicated reaction time as judged by TLC. b) In this case, 5 mol% of octacarbonyldicobalt and 10 mol% of $P(OPh)_3$ were used as catalyst. c) 7% of **1a** was recovered.



1 **4**

Table 3. Reactions of Various 1-Alkynylcyclopropanols

R in **1**	Reaction time/h	Yield of **4**/%[c]
Ph	2	91 (90)
C_6H_{13}	2.5	75 (71)
$CH_2OSiBu^tMe_2$	3	61 (61)
$CH_2CH_2OSiBu^tMe_2$	2	87 (81)
$SiMe_3$	3	68 (77)

a) Concentration of **1** is about 0.03 mol·dm^{-3}. b) Satisfactory NMR and IR spectra and elemental analysis and/or high resolution mass spectrum were obtained for each product. c) Yields in parentheses are those of the stoichiometric reactions.

mol% of $Co_2(CO)_8$ and 20 mol% of $P(OPh)_3$, **4a** was obtained in 91% yields, which is equal to the yield of the stoichiometric reaction. Even use of 5 mol% of $Co_2(CO)_8$ and 10 mol% of $P(OPh)_3$ promoted the reaction to give **4a** in 76% yield. In these reactions, the complex **3a** was observed during the reaction and $Co_2(CO)_4(P(OPh)_3)_2$ was thought to act as the real catalyst.

As the rearrangement was found to proceed catalytically in high yield by the addition of $P(OPh)_3$, the reactions of various 1-(1-alkynyl)cyclopropanols (**1**) were examined using 10 mol% of octacarbonyldicobalt and 20 mol% of $P(OPh)_3$, and the results were summarized in Table 3. Not only aryl-substituted alkyne derivatives, but also alkyl- or silyl-substituted alkyne derivatives gave the corresponding 3-substituted 2-cyclopentenones in good to high yields.

The authors would like to thank Professor Koichi Narasaka at the University of Tokyo for helpful discussions and encouragement during this study. The present work was partially supported by the Sumitomo Foundation.

References

1) N. Iwasawa, *Chem. Lett.*, **1992**, 473.
2) In the Pauson-Khand reaction, in which alkyne-cobalt complexes react with olefins to give cyclopentenones, efforts have been made to render the reaction to proceed catalytically. However, the efficiency was low probably due to the instability of $Co_2(CO)_6$ species liberated during the reaction. See; V. Rantenstrauch, P. Mégard, J. Canesa, and W. Küster, *Angew. Chem., Int. Ed. Engl.,* **29**, 1413 (1990), and references cited therein.
3) All the solvents employed were degassed before use. This precaution is important for the catalytic reactions. Otherwise **4a** was obtained in lower yield because of the instability of the catalyst **3a** to oxygen.
4) It was known that carbonyl ligands of alkyne-$Co_2(CO)_6$ complexes were easily replaced by one or two molecules of phosphines or phosphites. See; L. S. Chia, W. R. Cullen, M. Franklin, and A. R. Manning, *Inorg. Chem.*, **14**, 2521 (1975). Furthermore, in the case of $P(OPh)_3$, the complex **3a** was isolated and confirmed to be tetracarbonyl{1-(phenylethynyl)cyclopropanol}bis(triphenylphosphite)dicobalt by ^1H and ^{13}C-NMR; ^1H-NMR ($CDCl_3$) δ 1.48 (2H, dd, J=8.4, 3.9 Hz), 1.53 (2H, dd, J=8.4, 3.9 Hz), 3.46 (1H, s), 6.90 (12H, d, J=8.1 Hz), 7.10 (6H, t, J=7.3 Hz), 7.14-7.32 (15H, m), 7.65 (2H, d, J=7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 21.5, 57.9, 86.1, 97.9, 121.2, 124.8, 126.3, 128.0, 129.6, 131.2, 140.1, 151.2, 202.8, 203.4.
5) C. A. Tolman, *Chem. Rev.*, **3**, 313 (1977).

(Received March 18, 1993)