Octacarbonyldicobalt Promoted Transformation of 1-(1,2-Propadienyl)cyclopropanols to 1,4-Hydroquinones

Nobuharu Iwasawa, Yufu Owada, and Takeshi Matsuo
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113

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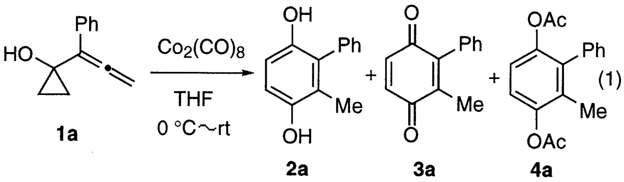
A novel transformation reaction of 1-(1,2-propadienyl)-cyclopropanols to 1,4-hydroquinone derivatives was developed utilizing the interaction of 1,2-propadienes and $Co_2(CO)_8$.

Utilization of 1,2-propadienes in transition metal promoted reactions has long been studied, however, use of octacarbonyldicobalt($Co_2(CO)_8$) for the reaction with 1,2-propadienes remains mostly unexplored. It has been reported that terminal 1,2-propadienes react with $Co_2(CO)_8$ to form unidentified complexes and excess 1,2-propadienes polymerize concurrently.[1] It has also been reported that a novel dimeric complex in which carbonyl ligand is inserted onto the central carbon of 1,2-propadiene is produced by the reaction of 1,2-propadiene itself with $Co_2(CO)_8$.[2] However, contrary to the well-known chemistry of alkyne-$Co_2(CO)_6$ complexes, these 1,2-propadiene-cobalt carbonyl complexes have rarely been applied to synthetic reactions probably due to their high catalytic activity to polymerize 1,2-propadienes.[1,3]

We have been studying the reactions of the transition metal complexes of strained molecules and have already reported that 1-(1-alkynyl)cyclopropanols rearrange to 2-cyclopentenones in good yield by the complexation with $Co_2(CO)_8$.[4] In this paper is described a novel transformation reaction of 1-(1,2-propadienyl)cyclopropanols to 1,4-hydroquinones utilizing the interaction of 1,2-propadienes and $Co_2(CO)_8$.

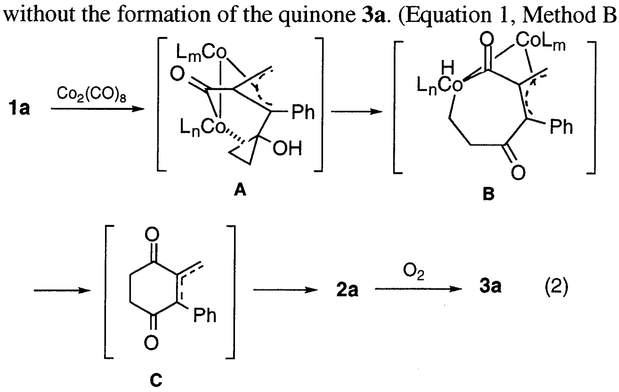
When 1-(1-phenyl-1,2-propadienyl)cyclopropanol **1a**[5] was treated with 1.1 molar amount of $Co_2(CO)_8$ in THF at 0 °C to rt under argon atmosphere, **1a** disappeared within several hours. Purification of the crude product revealed that 3-methyl-2-phenyl-1,4-hydroquinone **2a** and 3-methyl-2-phenyl-1,4-benzoquinone **3a** were produced in 35% and 20% yield respectively. (Equation 1, Method A)



	2a	**3a**	**4a**
Method A	35%	20%	-
Method B	-	-	53%

Method A: Products were isolated without acetylation.
Method B: Ac_2O and Et_3N were added to the reaction mixture.

The mechanism of the reaction is assumed as follows. (Equation 2) When **1a** is treated with $Co_2(CO)_8$, a carbonyl inserted intermediate **A**, the same type of complex as is proposed to be formed by the reaction of 1,2-propadiene itself with $Co_2(CO)_8$ by Nakamura,[2] is produced, although this complex is not observed by TLC during the reaction. The cyclopropane ring of this complex is effectively activated by the neighboring cobalt moiety and undergoes smooth ring expansion to give metallacyclic intermediate **B**, which gives **C** by reductive elimination. An unidentified intermediate was observed by TLC during the reaction and we at present suppose that this is the cyclohexadione derivative **C**, which could not be purified, but instead isomerized to the hydroquinone **2a** during work-up procedure. The benzoquinone **3a** is formed by oxidation of the hydroquinone **2a** with oxygen during purification. In order to avoid this oxidation and to simplify the purification of the product, we examined the work-up procedure and found that treatment of the reaction mixture with acetic anhydride and triethylamine gave an acetylated hydroquinone **4a** in 53% yield without the formation of the quinone **3a**. (Equation 1, Method B)



Examination of the reaction solvent revealed that ethyl acetate or ethereal solvents such as THF or diethyl ether gave good yield of the hydroquinone derivative **4a**. Furthermore, concentration of $Co_2(CO)_8$ had a significant effect on this reaction and under diluted conditions, the yield of the product increased to 76%. Interestingly, examination of the amount of the $Co_2(CO)_8$ revealed that a half molar amount of $Co_2(CO)_8$ is sufficient to

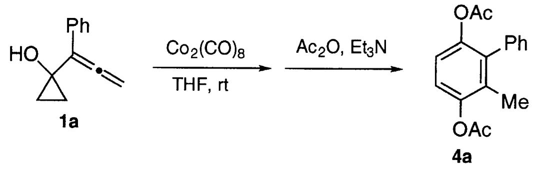


Table 1. Effect of the Concentration of the Reaction and Molar Amounts of $Co_2(CO)_8$

Molar Amounts of $Co_2(CO)_8$	Concentration /mol•dm^{-3}	Yield/%
1.10	0.10	53
1.10	0.03	69
1.10	0.01	76
0.26	0.03	50
0.56	0.03	70
2.20	0.03	73

promote the reaction. Thus, use of 0.56, 1.1 and 2.2 molar amounts of $Co_2(CO)_8$ all gave nearly the same yield of the product, while use of 0.26 molar amounts of $Co_2(CO)_8$ lowered the yield considerably. (Table 1) These results indicate that one molecule of $Co_2(CO)_8$ can transform two molecules of 1-(1,2-propadienyl)cyclopropanol, and a dimeric complex analogous to the one proposed by Nakamura[2] might be formed during the reaction.

As shown in Table 2, various 1- or 3-substituted 1,2-propadiene derivatives **1** were transformed into the 2-substituted or 2,3-disubstituted hydroquinone derivatives **4** in good yield. In particular, 1-(*t*-butyldimethylsilyl)-1,2-propadiene derivative **1d** gave high yield of the corresponding silylated hydroquinone **4d**, which is a useful intermediate for further manipulations.

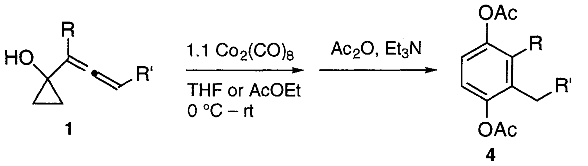


Table 2. Reactions of Various 1-(1,2-Propadienyl)-cyclopropanols

	R	R'	Solvent[a]	Reaction Conditions[b]	Yield/%
1a	Ph	H	THF	rt, 4 h	76
1b	Hex	H	AcOEt	rt, 1 h	60
1c	Me_3Si	H	THF	rt, 1 h	90[d]
1d[c]	Bu^tMe_2Si	H	AcOEt	rt, 2 d	87
1e	H	Ph	AcOEt	0 °C, 2 d	56
1f	H	Hex	THF	rt, 2 h	51

a) In most cases, THF and AcOEt gave nearly the same yields of the product **4**, and in this Table are shown better results. b) Concentration of the reaction is about 0.01 $mol\cdot dm^{-3}$. Reaction time indicates the time that starting material disappeared. c) In this case, the reaction was rather slow and 2.4 molar amounts of $Co_2(CO)_8$ was employed. d) In this case, the hydroquinone derivative **4c** was obtained in 47% yield and its desilylated derivative(R=R'=H) was obtained in 43% yield.

It should be noted that in the reactions of simple 1,2-propadienes such as 6-phenyl-1,2-hexadiene or 1,9-diphenyl-4,5-nonadiene with $Co_2(CO)_8$, smooth formations of yellowish complexes were observed at rt by TLC, which gave only unidentified, presumably polymerized, products on attempted isolation.[6] On the other hand, in the reactions of 1-(1,2-propadienyl)cyclopropanols with $Co_2(CO)_8$, no such complex formation was observed by TLC but the reaction proceeded smoothly at rt or below. These facts indicate that in this reaction, the rate determining step is the complex formation step and the successive ring expansion occurs rapidly. The presence of the cyclopropane ring close to the 1,2-propadiene moiety is therefore crucial to prevent the usually observed, undesired polymerization pathway.

In conclusion, a novel transformation reaction of 1-(1,2-propadienyl)cyclopropanols to hydroquinone derivatives is developed utilizing the interaction between 1,2-propadiene and $Co_2(CO)_8$. As benzoquinones and, in particular, naphthoquinones are widely seen in biologically active natural products,[7,8] this reaction affords a new method for the synthesis of such compounds starting from non-aromatic precursors.

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References and Notes

1 H. Greenfield, I. Wender, and J. H. Wotiz, *J. Org. Chem.*, **21**, 875 (1956). See also; E. A. Mushina, T. K. Makhina, I. Kiriya, S. D. Artamonova, Y. N. Dyshlevskii, B. A. Krentsel, and A. M. Taber, *Vysokomol. Soedin., Ser. B*, **26**, 654 (1984). *Chem. Abstracts*, **102**, 46292z (1985).

2 A. Nakamura, *Bull. Chem. Soc. Jpn.*, **39**, 543 (1966).

3 To our knowledge, the following two papers describe some transformation reactions using interaction between $Co_2(CO)_8$ and 1,2-propadienyl compounds. (a) Conversion of 1,1,3,3-tetraphenylpropadiene to indene derivatives: P-J. Kim and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **38**, 2022 (1965). (b) 1,3-H shift of 1,2-propadienes to 1,3-dienes: L. S. Trifonov, A. S. Orahovats, and H. Heimgartner, *Helv. Chim. Acta*, **70**, 1070 (1987). Reactions of acylcobalt complexes with 1,2-propadienes have also been reported. S. Gambarotta and H. Alper, *J. Org. Chem.*, **46**, 2142 (1981); L. S. Hegedus and Y. Inoue, *J. Am. Chem. Soc.*, **104**, 4917 (1982).

4 For pervious works, see: N. Iwasawa, *Chem. Lett.*, **1992**, 473; N. Iwasawa and T. Matsuo, *Chem. Lett.*, **1993**, 997; N. Iwasawa and M. Iwamoto, *Chem. Lett.*, **1993**, 1257.

5 Compounds **1a-1d** were prepared in one step in good yields by the reaction of the corresponding propargylaluminium reagent with iodomagnesium salt of cyclopropanone hemiacetal: G. Courtois, M. Harama, and L. Miginiac, *J. Organomet. Chem.*, **198**, 1 (1980); J. Salaun, F. Bennani, J. C. Compain, A. Fadel, and J. Ollivier, *J. Org. Chem.*, **45**, 4129 (1980). Compounds **1e** and **1f** were prepared from the TBS ethers of the corresponding 1-(1-alkenyl)cyclopropanols by the following procedure. i) dibromocyclopropanation by bromoform in the presence of potassium *t*-butoxide, ii) dehalogenation to give 1,2-propadiene derivative by treatment with MeLi, and iii) desilylation by treatment with TMSCl in MeOH. In most cases, these compounds are not very stable. We routinely store these compounds as TBS ethers at 0 °C and deprotect and purify them just before use.

6 K. Hayashi and N. Iwasawa, unpublished results.

7 R. H. Thomson, *Naturally Occurring Quinones:* 3rd ed.; Chapman and Hall: New York 1987.

8 Naphthoquinones are easily prepared from benzoquinones by the Diels-Alder reaction with butadiene derivatives followed by oxidation. For example, see; L. F. Fieser, *J. Am. Chem. Soc.* **70**, 3165 (1948); G. A. Kraus, J. Li, M.S. Gordon, J. H. Jensen, *J. Am. Chem. Soc.*, **115**, 1993 (1993). See also; K. T. Finley, In *The Chemistry of the Quinonoid Compounds* Vol. 2, Part 2; ed by S. Patai and Z. Rappoport, Wiley-Interscience: New York, 1988; p. 537.