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Transformation of 1-(1, 2-Propadienyl)cyclopropanols into Substituted Hydroquinones Employing Octacarbonyldicobalt

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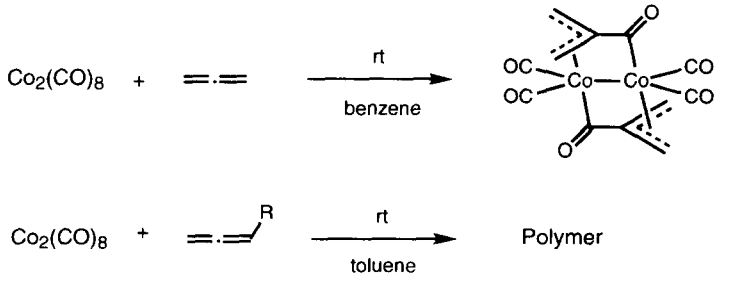
Abstract: A novel transformation of 1-(1,2-propadienyl)cyclopropanols into substituted 1,4-hydroquinones has been developed utilizing the interaction of 1,2-propadienes and octacarbonyldicobalt ($Co_2(CO)_8$). This reaction was applied to the synthesis of vitamin E and K analogs. © 1997 Elsevier Science Ltd.

INTRODUCTION

Utilization of 1,2-propadienes (allenes) in transition metal-promoted reactions has long been studied, however, in most of these reactions the 1,2-propadienes react simply as olefins.[1] Recently, several examples have appeared where the unique characteristics of the 1,2-propadiene system have been utilized for synthetic reactions. The most extensively studied have been the reactions between 1,2-propadienes and palladium(II) compounds to give π-allyl palladium intermediates,[2] and more recently several unique transformations have been achieved utilizing the complex formation between 1,2-propadienes and iron carbonyls.[3,4] On the other hand, use of octacarbonyldicobalt($Co_2(CO)_8$) in reactions involving 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 that excess 1,2-propadiene is polymerized concurrently.[5] It has also been reported that a novel dimeric complex, in which a carbonyl ligand has become connected to the central carbon of 1,2-propadiene, is produced by the reaction of 1,2-propadiene itself with $Co_2(CO)_8$.[6] (Scheme 1) However, unlike the well-known chemistry of alkyne-$Co_2(CO)_6$ complexes, these 1,2-propadiene-cobalt carbonyl

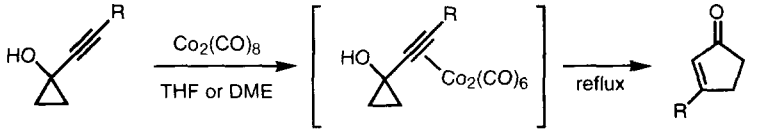


Scheme 1

This paper is dedicated to Professor Samuel J. Danishefsky in gratitude for stimulating and enjoyable experiences during my postdoctoral studies.

complexes have rarely been applied in synthetic reactions, probably due to their high activity in catalyzing the polymerization of 1,2-propadienes.[5,7]

We have already reported that 1-(1-alkynyl)cyclopropanols rearrange to 2-cyclopentenones in good yield *via* their alkyne-$Co_2(CO)_6$ complexes.[8] (Scheme 2) We presume that in this reaction the cobalt moiety provides effective activation for rearrangement of the cyclopropoyl ring, on account of their close proximity.



Scheme 2

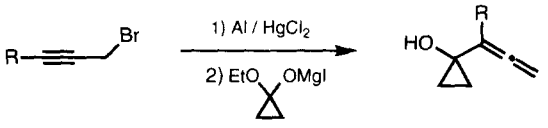
It was surmised that a similar proximity effect might well induce novel ring transformation reactions when cyclopropanols containing an allenic, instead of acetylenic, moiety are exposed to $Co_2(CO)_8$. This expectation was in fact realized. In this paper, we describe the conversion of 1-(1,2-propadienyl)cyclopropanols to 1,4-hydroquinone derivatives under the influence of $Co_2(CO)_8$, and the application of this chemistry to the synthesis of vitamin E and K analogs.[9]

RESULTS AND DISCUSSION

I. Preparation of 1-(1,2-propadienyl)cyclopropanols

Our first objective became the development of a preparative method for 1-(1,2-propadienyl)cyclopropanols possessing a substituent at positions 1 or 3 of the allenic unit. 1-(1-Alkynyl)cyclopropanols are generally prepared by the reaction of alkynyllithiums or alkynylmagnesium reagents with the iodomagnesium salt of cyclopropanone hemiacetal.[10] Accordingly, it was expected that 1-(1,2-propadienyl)cyclopropanols could be synthesized by the reaction of appropriate propargyl metallic reagents with the same hemiacetal. However, most propargyl metallic species, including the lithium, magnesium, titanium derivatives etc are known to be in equilibrium with propadienyl metallic species and to react with carbonyl compounds to give acetylenic alcohols as the major products.[11] In fact, the reaction of propargylmagnesium bromide with the iodomagnesium salt of cyclopropanone hemiacetal gave a mixture of acetylenic and propadienyl alcohols. However, it was found that the use of propargyl aluminum reagents, which are known to give propadienyl alcohols selectively on reaction with carbonyl compounds,[11,12] gave selectively 1-(1,2-propadienyl)cyclopropanols having a substituent at the 1-position of the propadienyl moiety.

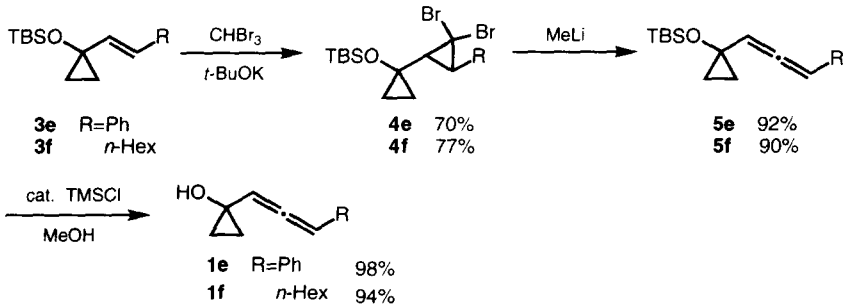
Thus, treatment of propargyl bromides **2a** - **2d** with powdered aluminum and a catalytic amount of mercuric chloride gave propargyl aluminum reagents,[12] and the reaction of these with the iodomagnesium salt of cyclopropanone hemiacetal gave the corresponding substituted 1-(1,2-propadienyl)cyclopropanols **1a** - **1d** in moderate to good yield (Scheme 3).



2a	R=Ph		**1a**	R=Ph	60%
2b	*n*-Hex		**1b**	*n*-Hex	30%
2c	Me_3Si		**1c**	Me_3Si	25%
2d	*t*-$BuMe_2Si$		**1d**	*t*-$BuMe_2Si$	68%

Scheme 3

As 1-(1,2-propadienyl)cyclopropanols having a substituent at the 3-position of the propadienyl moiety could not be synthesized by this procedure, they were prepared using the Skattebφl reaction of dibromocyclopropanes[13] prepared from the corresponding 1-(1-alkenyl)cyclopropanol derivatives. Thus, *t*-butyldimethylsilyl ethers of 1-(1-alkenyl)cyclopropanols **3e** and **3f** were prepared by the standard procedure, and dibromocyclopropanations were carried out by treatment with bromoform and potassium *t*-butoxide in pentane[14] to give **4**. Next, the Skattebφl reactions were carried out by treating **4** with methyllithium[14] to give the 1-(1,2-propadienyl)cyclopropanol derivatives **5** in good yield. **1e** and **1f** were obtained on deprotection of **5** with a catalytic amount of trimethylsilyl chloride (TMSCl) in methanol. (Scheme 4) As these 1-(1,2-propadienyl)cyclopropanols **1a** - **1f** were not very stable, they were usually kept at 0 °C as their *t*-butyldimethylsilyl ethers and were deprotected just before use.

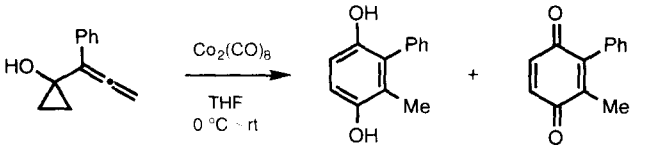


3e	R=Ph		**4e**	70%	
3f	*n*-Hex		**4f**	77%	
			5e	92%	
			5f	90%	
1e	R=Ph	98%			
1f	*n*-Hex	94%			

Scheme 4

II. Transformation of 1-(1,2-propadienyl)cyclopropanols to 1,4-hydroquinones employing octacarbonyldicobalt

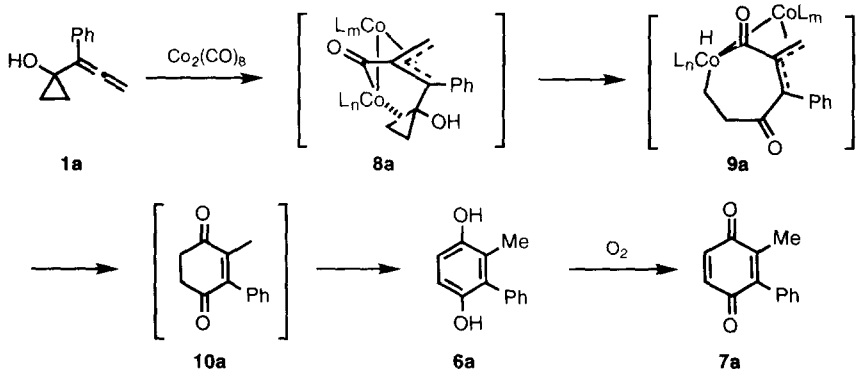
With a range of substrates now secured, we turned our attention to studying the reaction of 1-(1-phenyl-1,2-propadienyl)cyclopropanol **1a** with $Co_2(CO)_8$. When **1a** was treated with a 1.1 molar amount of $Co_2(CO)_8$ in THF from 0 °C to rt under an argon atmosphere, all the **1a** disappeared within a few hours. Purification of the crude product by silica gel chromatography revealed that 3-methyl-2-phenyl-1,4-hydroquinone **6a** and 3-methyl-2-phenyl-1,4-benzoquinone **7a** were produced in 35% and 20% yield respectively (Scheme 5).



1a **6a** 35% **7a** 20%

Scheme 5

A plausible mechanism for the reaction is as follows (Scheme 6). Combination of **1a** with $Co_2(CO)_8$ may lead to the carbonylated intermediate **8a**. A similar complex was proposed by Nakamura to result from reaction of 1,2-propadiene itself with $Co_2(CO)_8$.[6] This complex, however, is not detectable by TLC during the cource of the reaction. The cyclopropane ring in **8a**, now effectively activated by the cobalt moiety, undergoes ring expansion to give a metallacyclic intermediate **9a**, which is further transformed to **10a** by reductive elimination. An intermediate observed by TLC during the reaction was presumed to be cyclohexenedione **10a** (*vide infra*). At this time, however, we were not able to isolate this material, because it readily tautomerized to hydroquinone **6a** during work-up. Benzoquinone **7a** probably formed by air oxidation of **6a** during purification.



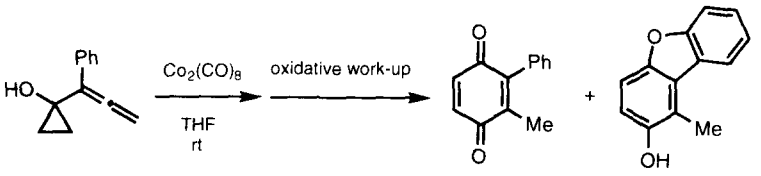
1a **8a** **9a** **10a** **6a** **7a**

Scheme 6

II.1. Examination of the reaction conditions

Initial efforts to optimize yields and reaction conditions focused on the development of a work-up procedure that might simplify isolation of the products. With this in mind, we explored oxidative quenching of the reaction with consequent formation of quinoid materials. Thus, 1-(1-phenyl-1,2-propadienyl)-cyclopropanol **1a** was treated with $Co_2(CO)_8$ in THF at rt under an argon atmosphere, and after **1a** had disappeared as determined by TLC, the reaction mixture was stirred under an oxygen atmosphere or was treated with triethylamine to accelerate the tautomerization of the intermediate **10a** to the hydroquinone **6a**, followed by treatment with aqueous iron(III) chloride solution. As shown in Scheme 7, benzoquinone **7a** was obtained selectively without the formation of hydroquinone **6a**. In both cases, however, the dibenzofuran **11** was obtained as a side-product in up to 11% yield. Although the exact reaction mechanism for the formation

of **11** is not clear, the substance is definitely formed during the oxidation reaction, because it was not formed when oxidative treatment was omitted.

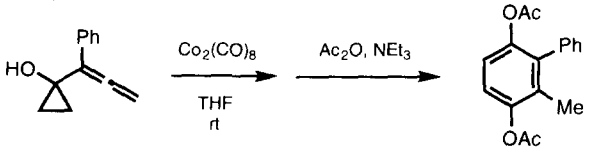


1a **7a** **11**

O_2 atmosphere	47%	trace
Et_3N then $FeCl_3$	46%	11%

Scheme 7

A much more successful work-up procedure that completely suppressed formation of side product **11** involved acetylation of the intermediate hydroquinone **6a**. Thus, addition of acetic anhydride and triethylamine to the reaction mixture after complete disappearance of **1a** furnished acetylated hydroquinone **12a** in 53% yield. (Scheme 8)

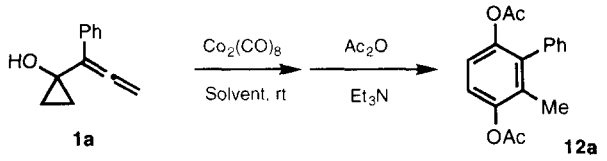


1a **12a** 53%

Scheme 8

We next investigated solvent effects. 1-(1-Phenyl-1,2-propadienyl)cyclopropanol **1a** was treated with $Co_2(CO)_8$ in various solvents, and after the disappearance of **1a**, acetic anhydride and triethylamine were added to the reaction mixture. As shown in Table 1, ethyl acetate and ethereal solvents such as THF gave good yields of the acetylated hydroquinone **12a**, while non-polar solvents such as toluene gave the product in low yield. In dichloromethane, **1a** was consumed, however, a complex mixture of products was obtained. Acetonitrile did not give the acetylated hydroquinone **12a** and the starting material **1a** was recovered in 45% yield. $Co_2(CO)_8$ probably formed catalytically inert complexes with acetonitrile faster than reaction with **1a** could occur.

As stated in the introduction, it has been reported that 1, 2-propadienes react with $Co_2(CO)_8$ to form unidentified complexes and that excess 1,2-propadiene polymerizes.[5] As the formation of unidentified oligomeric products was observed in the above reactions, we examined the effect of concentration of the reaction with the expectation that the formation of oligomers could be suppressed by carrying out the reaction under diluted conditions. As shown in Table 1, the yield of hydroquinone **12a** increased as the concentration was lowered, and when the reaction was conducted in 0. 01mol·dm^{-3} THF solution from 0 °C to rt, the acetylated hydroquinone **12a** was obtained in 78% yield.



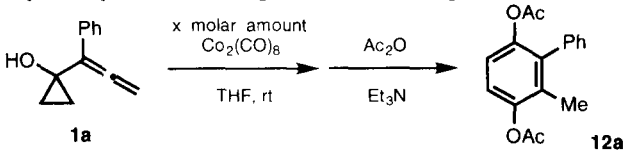
1a **12a**

Table I. Examination of the Reaction Solvent and Concentration.

Solvent	Concentration/mol·dm^{-3}	Yield/%
THF	0.1	53
	0.03	69
	0.01[a)]	78
Et_2O	0.03	40
DME	0.03	43
AcOEt	0.03	58
toluene	0.03	28
CH_2Cl_2	0.03	-
CH_3CN	0.03	-[b)]

a) The reaction was conducted at 0 °C to rt.
b) 45% of **1a** was recovered.

We also examined the effect of molar ratio of $Co_2(CO)_8$ to 1-(1,2-propadienyl)cyclopropanol **1a**, and found that a half molar amount of $Co_2(CO)_8$ is sufficient to promote the reaction. Thus, experiments using 0.56, 1.1, and 2.2 molar amounts of $Co_2(CO)_8$ gave nearly the same yield of product, while use of only 0.26 molar amounts of $Co_2(CO)_8$ lowered the yield considerably (Table 2). These results indicate that one molecule of $Co_2(CO)_8$ can transform two molecules of the cyclopropanol **1a**, and that a dimeric complex analogous to the one proposed by Nakamura[6] might be formed during the reaction.



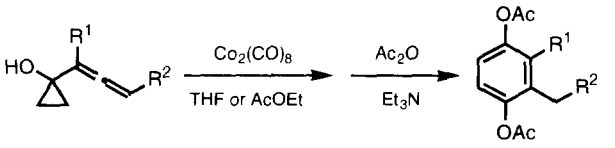
1a **12a**

Table 2. Examination of the Molar Ratio.

Mole ratio($Co_2(CO)_8$: **1a** = x : 1)	Yield/%
0.26	50
0.56	70
1.1	69
2.2	73

II.2. Examination of the generality of the reaction

Various 1-(1,2-propadienyl)cyclopropanols having a substituent at the 1- or 3-position of the propadienyl moiety **1a** - **1f** were synthesized as already described in Section I, and were reacted with 1.1 mole amounts of $Co_2(CO)_8$ in either THF or ethyl acetate. As summarized in Table 3, the reactions proceeded smoothly at 0 °C to rt, and the various 1-(1,2-propadienyl)cyclopropanols **1** were transformed into the corresponding 2-mono-substituted or 2, 3-disubstituted 1,4-hydroquinone derivatives **12a** - **12f** in good yield. In particular, 1-(1,2-propadienyl)-cyclopropanols having a trimethylsilyl or *t*-butyldimethylsilyl group at the 1-position of the 1,2-propadienyl moiety gave a good yield of product. Thus, while the trimethylsilyl derivative **1c** gave a mixture of silylated hydroquinone **12c** and its desilylated derivative **12c'** in a total yield of 90%, the corresponding *t*-butyldimethylsilyl derivative **1d** gave a high yield of the silylated hydroquinone **12d** as the sole product.

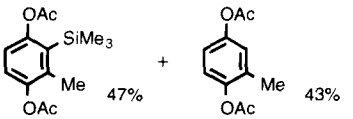


1 **12**

Table 3. Generality of the Reaction.

Substrate	R^1	R^2	Solvent	Reaction Conditions	Yield/%
1a	Ph	H	THF	rt, 4 h	78
1b	Hex	H	AcOEt	rt, 1 h	60
1c	Me_3Si	H	THF	rt, 1 h	90 *)
1d	*t*-$BuMe_2Si$	H	AcOEt	rt, 2 d	87
1f	H	Ph	AcOEt	0 °C, 2 d	56
1g	H	Hex	THF	rt, 2h	51

*)

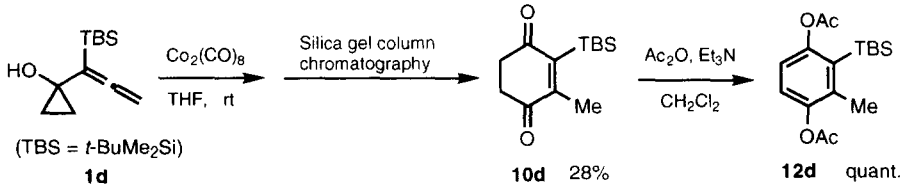


12c **12c'**

II.3. Isolation of the intermediate 2-cyclohexene-1,4-dione

As already mentioned, when 1-(1-phenyl-1,2-propadienyl)cyclopropanol **1a** was treated with $Co_2(CO)_8$ in THF, an intermediate could be identified by TLC but this disappeared gradually as the hydroquinone **6a** was formed. As was also observed during the examination of the work-up procedure, when the reaction mixture of **1a** and $Co_2(CO)_8$ was treated with iron(III) chloride solution without triethylamine, hydroquinone **6a** was obtained along with benzoquinone **7a**. These facts strongly suggest that the intermediate 2-cyclohexene-1,4-dione derivative can exist for a relatively long period before tautomerizing into the corresponding hydroquinone.[15]

Consequently, we tried to isolate this intermediate employing several kinds of 1-(1,2-propadienyl)cyclopropanols as reaction substrates. When the *t*-butyldimethylsilyl derivative **1d** was used, the intermediate could be isolated after a careful manipulation. Thus, **1d** was treated with $Co_2(CO)_8$ in THF at rt for 1 day and the reaction mixture was subjected to silica gel column chromatography (silica deactivated by 10% amount of water). The purification was performed as quickly as possible so that tautomerization of the intermediate would be minimized, and the expected cyclohexenedione **10d** (2-*t*-butyldimethylsilyl-3-methyl-2-cyclohexene-1,4-dione) was isolated in 28% yield, along with recovered **1d** (11%), the hydroquinone **6d** (22%) and the benzoquinone **7d** (18%) (Scheme 9).



(TBS = *t*-BuMe$_2$Si)

1d **10d** 28% **12d** quant.

10d: ^{1}H NMR($CDCl_3$) δ = 0.21(6H, s), 0.92(9H, s), 2.04(3H, s), 2.84(4H, s).
^{13}C NMR($CDCl_3$) δ = -1.9, 17.3, 18.5, 27.4, 36.8, 39.2, 152.3, 156.9, 197.4, 202.3.
IR(neat) 1680 cm^{-1}.

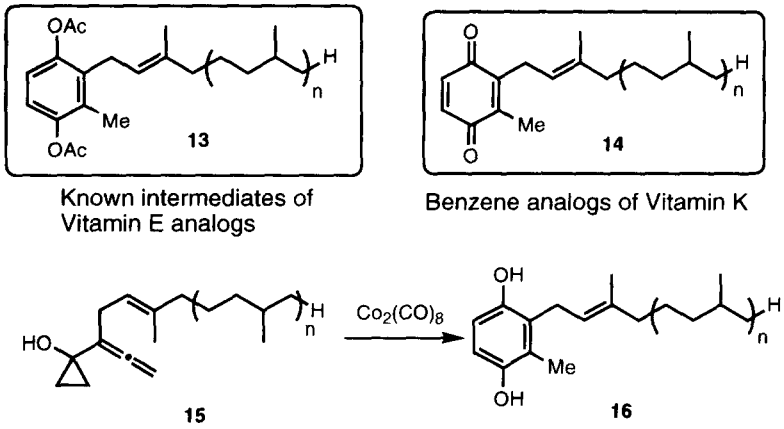
Scheme 9

The ^{1}H NMR, ^{13}C NMR and IR spectral data support 2-cyclohexene-1,4-dione structure for compound **10d**. The ^{13}C NMR spectrum of **10d** shows the presence of the two carbonyl carbons at chemical shifts of 197.4 and 202.3 ppm, and of two olefinic carbons at 152.3 and 156.9 ppm. An absorbance at 1680 cm^{-1} in the IR spectrum agrees with the presence of an α,β-unsaturated ketone. Furthermore, when this intermediate was treated with triethylamine and acetic anhydride in dichloromethane, the tautomerization and acetylation reactions proceeded smoothly at rt to give the hydroquinone diacetate **12d** quantitatively. These results support the assumption that the reaction proceeds *via* the intermediate **10** when 1-(1,2-propadienyl)cyclopropanol **1** is treated with $Co_2(CO)_8$. (Scheme 6)

III. Synthesis of vitamin E and vitamin K analogs

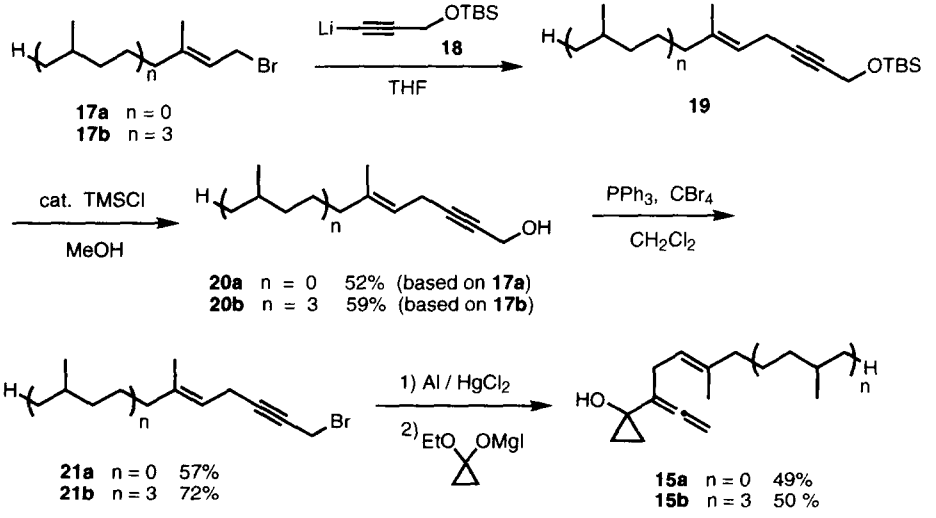
We next applied this reaction to the synthesis of quinonoid natural compounds.[16] We chose vitamins E and K analogs **13** and **14** as target molecules, to be constructed using our reaction in a one-step procedure.

It was expected that employment of 1-(1,2-propadienyl)cyclopropanols **15** with a polyprenyl substituent at the 1-position of the propadienyl moiety in the reaction with $Co_2(CO)_8$ would result in the formation of hydroquinones **16** having the basic structure of vitamin E and K analogs. Subsequent treatment of **16** with acetic anhydride would give hydroquinone diacetates **13**, which are known synthetic intermediates of vitamin E analogs.[17] Oxidative treatment of **16** would give 2,3-disubstituted benzoquinones **14**, benzene analogs of vitamin K as shown in Scheme 10.



Scheme 10

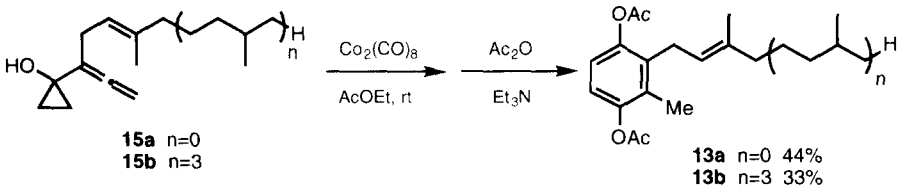
1-[1-(3-Methylbut-2-enyl)-1,2-propadienyl]cyclopropanol [1-(1-prenyl-1,2-propadienyl)cyclopropanol] **15a** and 1-[1-(3,7,11,15-tetramethylhexadec-2-enyl)-1,2-propadienyl]cyclopropanol [1-(1-phytyl-1,2-propadienyl)cyclopropanol] **15b** were prepared according to the procedure shown in Scheme 11. Alkylation of 3-*t*-butyldimethylsiloxy-1-propynyllithium **18** with prenyl bromide **17a** or phytyl bromide **17b** gave the alkylation products **19** in good yield, and the crude products were directly desilylated with a catalytic amount of trimethylsilyl chloride in methanol to give the propargyl alcohols **20a** and **20b**. Bromination of the propargyl alcohols was carried out cleanly by the use of triphenylphosphine and carbon tetrabromide, giving the corresponding bromides **21a** and **21b**.



Scheme 11

The resulting propargyl bromides **21a** and **21b** were converted to the corresponding aluminum reagents by reaction with powdered aluminum and a catalytic amount of mercuric chloride.[12] Then the iodomagnesium salt of cyclopropanol hemiacetal was treated with these reagents affording 1-(1-prenyl-1,2-propadienyl)cyclopropanol **15a** and 1-(1-phytyl-1,2-propadienyl)cyclopropanol **15b** in 49% and 50% yield, respectively.

When 1-(1-prenyl-1,2-propadienyl)cyclopropanol **15a** was treated with $Co_2(CO)_8$ in ethyl acetate at rt, it had disappeared within 2 h, and acetic anhydride and triethylamine were then added to the reaction mixture. After purification, the desired acetylated hydroquinone **13a**, a known vitamin E analog intermediate,[17] was obtained in 44% yield. For 1-(1-phytyl-1,2-propadienyl)cyclopropanol **15b**, the reaction was carried out the same way as for **15a**, and the corresponding acetylated hydroquinone **13b**, which is also a known vitamin E analog intermediate,[17] was obtained in 33% yield. (Scheme 12).

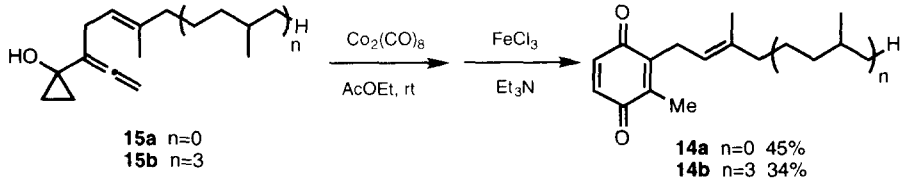


15a n=0
15b n=3

13a n=0 44%
13b n=3 33%

Scheme 12

We next tried to prepare benzene analogs of vitamin K by carrying out the quenching oxidatively. 1-(1-Prenyl-1,2-propadienyl)cyclopropanol **15a** was treated with $Co_2(CO)_8$ in ethyl acetate at rt and after the disappearance of **15a**, triethylamine was added followed by the addition of iron(III) chloride solution. After chromatographic purification, 2-methyl-3-(3-methylbut-2-enyl)-*p*-benzoquinone **14a**, a benzoquinone analog of vitamin $K_2(5)$, was obtained in 45% yield. The same reaction using 1-(1-phytyl-1,2-propadienyl)-cyclopropanol **15b** gave the corresponding benzoquinone **14b**, a benzoquinone analog of vitamin K_1, in 34% yield. (Scheme 13) Thus, either vitamin E or vitamin K analogs could be obtained by appropriate choice of the quenching conditions.



15a n=0
15b n=3

14a n=0 45%
14b n=3 34%

Scheme 13

IV. Summary

In summary, a novel transformation reaction of 1-(1,2-propadienyl)cyclopropanols to hydroquinone derivatives has been developed utilizing the interaction of 1,2-propadienes and $Co_2(CO)_8$.[21] The reaction proceeds smoothly at rt and subsequent treatment with acetic anhydride and triethylamine gives the acetates of 2-substituted or 2,3-disubstituted hydroquinones in good yield. Furthermore, this reaction has been applied to the synthesis of vitamin K and vitamin E analogs.

EXPERIMENTAL

General. All operations were performed under an argon atmosphere. Tetrahydrofuran(THF) and diethyl ether were distilled from benzophenone ketyl. Dichloromethane was distilled from P_2O_5 and then from CaH_2 and stored over MS 4A. Toluene and pentane were distilled from $CaCl_2$ and stored over MS 4A. Ethyl acetate was washed with 5% sodium carbonate solution and brine and dried over anhydrous sodium sulfate, then distilled and stored over MS 4A. Solvents used for the $Co_2(CO)_8$ promoted reactions were degassed with sonication just before use. $Co_2(CO)_8$ was purchased from Kanto Chemicals. ^1H NMR (500 MHz) spectra were recorded on a Bruker AM 500 spectrometer in $CDCl_3$ solution using chloroform (δ=7.24) as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JMS-SX102A mass spectrometer at an ionization energy of 70 eV. Melting points were uncorrected. Reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica-gel plates (Merck Kieselgel 60 F-254 Art. 5715). Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art. 7734. Preparative TLC (silica gel) was performed with Wakogel B-5F.

Preparation of 1-(1,2-propadienyl)cyclopropanols 1a - 1d.

The preparation of **1a** is described as a representative procedure. 1-Bromo-3-phenyl-2-propyne (**2a**),[18] 1-bromo-2-nonyne (**2b**)[19] and 1-bromo-3-trimethylsilyl-2-propyne (**2c**)[20] were prepared according to the literature. 1-Bromo-3-*t*-butyldimethylsilyl-2-propyne (**2d**) was prepared in a similar manner to the literature for 1-bromo-3-trimethylsilyl-2-propyne (**2c**).[20]

1-Bromo-3-*t*-butyldimethylsilyl-2-propyne (2d).
IR (neat) 2954, 2858, 1254, 1038, 833 cm^{-1}; ^1H NMR δ = 0.09 (6H, s), 0.92 (9H, s), 3.89 (2H, s); Anal. Calcd for $C_9H_{17}BrSi$: C, 46.35; H, 7.35%, Found: C, 46.16; H, 7.14%.

1-(1-Phenyl-1,2-propadienyl)cyclopropanol (1a).

A suspension of powdered aluminum (295 mg, 10.9 mmol) and mercuric chloride (100 mg) in THF (1 mL) was refluxed for 30 minutes. After the mixture was cooled to rt, a THF solution (6 mL) of 1-bromo-3-phenyl-2-propyne (3.19 g, 16.4 mmol) was added dropwise to the suspension and the mixture was further stirred at rt overnight. In another flask, a diethyl ether solution (35 mL) of 1-ethoxycyclopropanol (1.63 g, 16.0 mmol) was added dropwise to a diethyl ether solution of methylmagnesium iodide (2.2 M solution, 7.4 ml, 16.3 mmol) at 0 °C, and then the mixture was warmed to rt. The above propargyl aluminum reagent was added to the diethyl ether suspension of the iodomagnesium salt of cyclopropanol hemiacetal at 0 °C. After the mixture had been stirred at rt for 7 hours, it was quenched with pH7 phosphate buffer, and the organic materials were extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography to give 1-(1-phenyl-1, 2-propadienyl)cyclopropanol (**1a**) in 60 % yield; IR (neat) 3413(br), 1938, 1232, 764, 696 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.88 - 0.90 (2H, m), 1.12 - 1.14 (2H, m), 2.22 (1H, brs), 5.12 (2H, s), 7.23 (1H, t, J = 7.4 Hz), 7.35 (2H, t, J = 7.7 Hz), 7.63 (2H, d, J = 7.9 Hz); HRMS Calcd for $C_{12}H_{12}O$: 172.0888, Found: 172.0869.

1-(1-Hexyl-1,2-propadienyl)cyclopropanol (1b) was prepared in the same manner as **1a**. Yield 30%; IR (neat) 3284(br), 2925, 1955, 1213, 847 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.72 - 0.74 (2H, m), 0.86 (3H, t, J = 6.9 Hz), 0.89 - 0.91 (2H, m), 1.22 - 1.34 (6H, m), 1.42 - 1.48 (2H, m), 2.01 (2H, tt, J = 3.5, 7.4 Hz), 2.06 (1H, brs), 4.78 (2H, t, J = 3.5 Hz); HRMS Calcd for $C_{12}H_{20}O$: 180.1515, Found: 180.1521.

1-(1-Trimethylsilyl-1,2-propadienyl)cyclopropanol (1c) was prepared in the same manner as **1a**. Yield 25%; IR (neat) 3324(br), 2958, 1928, 1247, 845 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.17 (9H, s), 0.71 - 0.73

(2H, m), 0.89 - 0.91 (2H,m), 2.01 (1H, brs), 4.42 (2H, s); HRMS Calcd for $C_9H_{16}OSi$: 168.0970, Found: 168.0963.

1-(1-*t*-Butyldimethylsilyl-1,2-propadienyl)cyclopropanol (1d) was prepared in the same manner as **1a**. Yield 68%; IR (neat) 3373(br), 2954, 2929, 1925, 1248, 833 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.15 (6H, s), 0.73 - 0.76 (2H, m), 0.89 - 0.90 (2H, m), 0.93 (9H, s), 1.97 (1H, brs), 4.42 (2H, s); HRMS Calcd for $C_{12}H_{22}OSi$: 210.1441, Found: 210.1439.

Preparation of 1-(1,2-propadienyl)cyclopropanols 1e and 1f.

Preparation of 1-*t*-Butyldimethylsiloxy-1-(2-phenylethenyl)cyclopropane (3e).

2-*t*-Butyldimethylsiloxy-4-phenyl-1,3-butadiene.

To a THF solution (20 mL) of diisopropylamine (4.02 g, 39.8 mmol) was added dropwise a hexane solution of *n*-butyllithium (1.6M solution, 25 ml, 40 mmol) at -78 °C. After the mixture had been stirred for 30 minutes, a THF solution (8 mL) of benzalacetone (5.5 g, 37.8 mmol) was added dropwise. Then a THF solution (10 mL) of *t*-butyldimethylsilyl chloride (6.86 g, 45.4 mmol) and hexamethylphosphoric triamide (14.3 g, 80 mmol) were added successively. After being stirred for 1.5 hours, the reaction mixture was quenched with pH7 phosphate buffer and the product was extracted with hexane three times. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, yielding 2-*t*-butyldimethylsiloxy-4-phenyl-1,3-butadiene in 38% yield; IR (neat) 2954, 2858, 1589, 1327, 1024, 833 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.20 (6H, s), 1.00 (9H, s), 4.40 (1H, s), 4.43 (1H, s), 6.56 (1H, d, J = 15.7 Hz), 6.84 (1H, d, J = 15.7 Hz), 7.21 (1H, t, J = 7.5 Hz), 7.30 (2H, t, J = 7.5 Hz), 7.39 (2H, d, J = 7.5 Hz); HRMS Calcd for $C_{16}H_{24}OSi$: 260.1596, Found: 260.1609.

1-*t*-Butyldimethylsiloxy-1-(2-phenylethenyl)cyclopropane (3e).

To a diethyl ether solution (3 mL) of 1-*t*-butyldimethylsiloxy-4-phenyl-1,3-butadiene (1.0 g, 3.8 mmol) was added a diethyl ether solution of diethylzinc(1 M solution, 5.8 ml, 5.8 mmol) and diiodomethane(1.6 g, 5.8 mmol) at rt. After the mixture had been refluxed for 3.5 hours, the reaction was quenched with pH7 phosphate buffer and the organic materials were extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified with silica gel column chromatography to give 1-*t*-butyldimethylsiloxy-1-(2-phenylethenyl)cyclopropane (**3e**) in 69% yield; IR (neat) 2954, 2858, 1300, 1036, 837 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.14 (6H, s), 0.82 - 0.85 (2H, m), 0.91 (9H, s), 1.08 - 1.11 (2H, m), 5.99 (1H, d, J = 15.8 Hz), 6.55 (1H, d, J = 15.8 Hz), 7.17 (1H, t, J = 7.1 Hz), 7.26 - 7.32 (4H, m); HRMS Calcd for $C_{17}H_{26}OSi$: 274.1753, Found: 274.1769.

Preparation of 1-*t*-Butyldimethylsiloxy-1-(1-octenyl)cyclopropane (3f).

1-(1-Octynyl)cyclopropanol was prepared according to the literature[10]; bp 86 °C / 0.7 mmHg; IR (neat) 3321(br), 2931, 2237, 1460 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.85 (3H, t, J = 7.0 Hz), 0.87 - 0.89 (2H, m), 0.98 - 1.00 (2H, m), 1.21 - 1.36 (6H, m), 1.44 - 1.48 (2H, m), 2.16 (2H, t, J = 7.2 Hz), 2.48 (1H, s); HRMS Calcd for $C_{11}H_{18}O$: 166.1358, Found: 166.1359.

1-(1-Octenyl)cyclopropanol.

To a THF suspension (20 mL) of lithium aluminum hydride (1.0 g, 3.8 mmol) was added a THF solution (15 mL) of 1-(1-octynyl)cyclopropanol (1.31 g, 7.89 mmol) at 0 °C. After the mixture had been refluxed for 2 hours, the reaction was quenched with saturated sodium sulfate. The organic layer was

decanted and extracted thoroughly with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography, yielding 1-(1-octenyl)cyclopropanol in 90% yield; IR (neat) 3273(br), 2922, 1460, 1290, 966 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.64 - 0.67 (2H, m), 0.86 (3H, t, J = 6.9 Hz), 0.96 - 0.99 (2H, m), 1.23 - 1.37 (8H, m), 2.00 (1H, brs), 2.01 - 2.05 (2H, m), 5.25 (1H, dt, J = 1.3, 15.4 Hz), 5.65 (1H, dt, J= 6.9, 15.4 Hz); HRMS Calcd for $C_{11}H_{20}O$: 168.1515, Found: 168.1538.

1-*t*-Butyldimethylsiloxy-1-(1-octenyl)cyclopropane (3f).

To a dichloromethane solution (20 mL) of 1-(1-octenyl)cyclopropanol (1.21 g, 7.17 mmol) was added triethylamine (2.6 mL) and *t*-butyldimethylsilyl triflate (2.90 g, 11.0 mmol) at 0 °C. The reaction was immediately quenched with pH7 phosphate buffer and the organic materials were extracted with ethyl acetate twice. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography, yielding 1-*t*-butyldimethylsiloxy-1-(1-octenyl)cyclopropane (**3f**) in 90% yield; IR (neat) 2927, 1466, 1254, 1034, 837 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.08 (6H, s), 0.63 - 0.65 (2H, m), 0.85 - 0.87 (12H, m), 0.89 - 0.92 (2H, m), 1.23 - 1.37 (8H, m), 1.99 (2H, q, J =6.8 Hz)), 5.29 (1H, d, J = 15.3 Hz), 5.56 (1H, dt, J = 6.8, 15.3 Hz,); HRMS Calcd for $C_{17}H_{34}OSi$: 282.2379, Found: 282.2365.

1-*t*-Butyldimethylsiloxy-2',2'-dibromo-3'-phenylbicyclopropane (4e).

To a pentane suspension (15 mL) of potassium *t*-butoxide (5.48 g, 48.8 mmol) was added dropwise a pentane solution (25 mL) of 1-*t*-butyldimethylsiloxy-1-(2-phenylethenyl)cyclopropane (**3e**)(1.73 g, 6.31 mmol) at 0 °C, and bromoform (7.92 g, 31.3 mmol) was successively added dropwise over an hour. After the mixture had been stirred at rt for about 2 hours, it was quenched with pH7 phosphate buffer and the product was extracted with diethyl ether. The organic layer was washed with saturated ammonium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, yielding 1-*t*-butyldimethylsiloxy-2',2'-dibromo-3'-phenylbicyclopropane (**4e**) in 70% yield; IR (neat) 2954, 1462, 1228, 1038, 835 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.17 (3H, s), 0.26 (3H, s), 0.59 - 0.62 (1H, m), 0.71 - 0.74 (1H, m), 0.90 - 0.91 (2H, m), 0.92 (9H, s), 2.45 (1H, d, J = 8.6 Hz), 2.49 (1H, d, J = 8.6 Hz), 7.21 (2H, d, J = 7.6 Hz), 7.28 - 7.36 (3H, m); Anal. Calcd for $C_{18}H_{26}OBr_2Si$: C, 48.44; H, 5.87%, Found: C, 48.35; H, 5.76%.

1-*t*-Butyldimethylsiloxy-2',2'-dibromo-3'-hexylbicyclopropane (4f) was prepared in the same manner as **4e**. Yield 77%; IR (neat) 2925, 1462, 1232, 1034, 835 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.12 (3H, s), 0.21 (3H, s), 0.44 - 0.47 (1H, m), 0.52 - 0.56 (1H, m), 0.78 - 0.80 (1H, m), 0.87 (3H, t, J = 7.1 Hz), 0.89 (9H, s), 0.99 - 1.04 (1H, m), 1.24 - 1.39 (10H, m), 1.56 - 1.61 (1H, m), 1.71 (1H, d, J = 8.1 Hz); HRMS Calcd for $C_{18}H_{34}O\ ^{79}Br\ ^{81}BrSi$: 454.0725, Found: m/z 454.0745.

1-*t*-Butyldimethylsiloxy-1-(3-phenyl-1,2-propadienyl)cyclopropane (5e).

To a diethyl ether solution (13 mL) of 1-*t*-butyldimethylsiloxy-2',2'-dibromo-3'-phenylbicyclopropane (**4e**)(1.79 g, 4.01 mmol) was added a diethyl ether solution of methyllithium(1 M solution, 6.5 ml, 6.5 mmol) at -78 °C and the mixture was warmed to 0 °C. After this mixture had been stirred for 20 minutes, the reaction was quenched with pH7 phosphate buffer and the organic materials were extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography, yielding 1-*t*-butyldimethylsiloxy-1-(3-phenyl-1, 2-propadienyl)cyclopropane (**5e**) in 92% yield; IR (neat) 2954, 1951, 1205, 1034, 837 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.10 (3H, s), 0.13 (3H, s), 0.76 - 0.77 (2H, m), 0.83 (9H, s), 0.96 - 0.97 (2H, m), 5.79 (1H, d, J = 6.4 Hz), 6.25 (1H, d, J = 6.4 Hz), 7.17 (1H, t, J = 7.0 Hz), 7.23 - 7.29 (4H, m); HRMS Calcd for $C_{18}H_{26}OSi$: 286.1753, Found: 286.1724.

1-*t*-Butyldimethylsiloxy-1-(1,2-nonadienyl)cyclopropane (5f) was prepared in the same manner as **5e**. Yield 90%; IR (neat) 2929, 1963, 1207, 1032, 837 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.10 (3H, s), 0.11 (3H, s), 0.65 - 0.68 (2H, m), 0.84 (9H, s), 0.83 - 0.88 (5H, m), 1.23 - 1.31 (6H, m), 1.35 - 1.38 (2H, m), 1.94 - 1.98 (2H, m), 5.20 (1H, q, J = 6.6Hz), 5.34 (1H, dt, J = 3.0, 6.5 Hz); HRMS Calcd for $C_{18}H_{34}OSi$: 294.2378, Found: m/z 294.2368.

1-(3-Phenyl-1,2-propadienyl)cyclopropanol (1e).

To a methanol solution (3 mL) of 1-*t*-butyldimethylsiloxy-1-(3-phenyl-1,2-propadienyl)cyclopropane (**5e**)(175 mg, 0.612 mmol) was added 5 drops of trimethylsilyl chloride at rt. After being stirred for 15 minutes, the reaction mixture was quenched with 8 drops of triethylamine and the solvent was removed under reduced pressure. The residue was purified by preparative TLC (hexane : ethyl acetate = 3 : 1), yielding 1-(3-phenyl-1,2-propadienyl)cyclopropanol (**1e**) in 98% yield; IR (neat) 3330(br), 1948, 1200, 781, 671 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.77 - 0.81 (2H, m), 1.07 - 1.08 (2H, m), 2.19 (1H, s), 5.64 (1H, d, J = 6.4 Hz), 6.38 (1H, d, J = 6.4 Hz), 7.19 - 7.21 (1H, m), 7.29 - 7.30 (4H, m); HRMS Calcd for $C_{12}H_{12}O$: 172.0888, Found: 172.0894.

1-(1,2-Nonadienyl)cyclopropanol (1f) was prepared in the same manner as **1e**. Yield 96%; IR (neat) 3288(br), 2925, 1963, 1460, 1201 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.61 - 0.67 (2H, m), 0.85 (3H, t, J = 7.0 Hz), 0.95 - 0.97 (2H, m), 1.22 - 1.32 (6H, m), 1.34 - 1.40 (2H, m), 1.97 - 2.02 (2H, m), 2.38 (1H, brs), 5.17 (1H, dt, J = 2.9, 6.5 Hz), 5.33 (1H, q, J = 6.5Hz); HRMS Calcd for $C_{12}H_{20}O$: 180.1515, Found: 180.1490.

Transformation of 1-(1,2-propadienyl)cyclopropanols 1a - 1f to hydroquinone derivatives 12a - 12f employing $Co_2(CO)_8$.

2-*t*-Butyldimethylsilyl-3-methyl-*p*-phenylene diacetate (12d).

To an AcOEt solution (9 mL) of $Co_2(CO)_8$ (145 mg, 0.425 mmol) was added dropwise an AcOEt solution (10 mL) of 1-(1-*t*-butyldimethylsilyl-1,2-propadienyl)cyclopropanol (**1d**) (37.6 mg, 0.179 mmol) over 10 minutes at rt. The mixture was stirred for about 2 days, and after disappearance of **1d** was confirmed by TLC, acetic anhydride (1 mL), triethylamine (1 mL) and a catalytic amount of dimethylaminopyridine were added. The mixture was quenched with pH7 phosphate buffer and organic materials were extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified with preparative TLC (hexane : ethyl acetate = 5 : 1) to give 2-*t*-butyldimethylsilyl-3-methyl-*p*-phenylene diacetate (**12d**) in 87% yield; mp 83 °C; IR (KBr disk) 2929, 1759, 1367, 1228 1192 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.35 (6H, s), 0.92 (9H, s), 2.21 (3H, s), 2.26 (3H, s), 2.29 (3H, s), 6.89 (1H, d, J = 8.8 Hz), 7.00 (1H, d, J = 8.8 Hz); Anal. Calcd for $C_{17}H_{26}O_4Si$: C, 63.32; H, 8.13%, Found: C, 63.08; H, 7.93%.

2-Methyl-3-phenyl-*p*-phenylene diacetate (12a) was prepared in the same manner as **12d**. Yield 78%; IR (neat) 1761, 1369, 1194, 1157 cm^{-1}; ^1H NMR($CDCl_3$) δ = 1.85 (3H, s), 1.91 (3H, s), 2.31 (3H, s), 6.96 (1H, d, J = 8.7 Hz), 7.04 (1H, d, J = 8.7 Hz), 7.16 - 7.17 (2H, m), 7.32 - 7.35 (1H, m), 7.37 - 7.40 (2H, m); Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%, Found: C, 71.64; H, 5.79%.

2-Hexyl-3-methyl-*p*-phenylene diacetate (12b) was prepared in the same manner as **12d**. Yield 60%; IR (neat) 2927, 1765, 1369, 1215, 1184 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.87 (3H, t, J = 6.8 Hz), 1.28 - 1.43 (8H, m), 2.10 (3H, s), 2.29 (3H, s), 2.30 (3H, s), 2.48 - 2.51 (2H, m), 6.85 (1H, d, J = 9.3 Hz), 6.87 (1H, d, J = 9.3 Hz); Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27%, Found: C, 70.02; H, 8.26%.

2-Methyl-3-trimethylsilyl-*p*-phenylene diacetate (12c) and **2-Methyl-*p*-phenylene diacetate (12c')** were prepared in the same manner as **12d**.
12c: Yield 47%; IR (neat) 2960, 1762, 1369, 1190, 849 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.33 (9H, s), 2.22 (3H, s), 2.26 (3H, s), 2.29 (3H, s), 6.84 (1H, d, J = 8.6 Hz), 6.99 (1H, d, J = 8.6 Hz); Anal. Calcd for $C_{14}H_{20}O_4Si$: C, 59.97; H, 7.19%, Found: C, 59.85; H, 7.05%. **12c'**: Yield 43%; IR (neat) 2931, 1761, 1371, 1215, 1173, 912 cm^{-1}; ^1H NMR($CDCl_3$) δ = 2.15 (3H, s), 2.26 (3H, s), 2.29 (3H, s), 6.90 (1H, dd, J = 2.6, 8.6 Hz), 6.95 (1H, d, J = 2.6 Hz), 6.99 (1H, d, J = 8.6 Hz); Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%, Found: C, 63.30; H, 5.78%.

2-Benzyl-*p*-phenylene diacetate (12e) was prepared in the same manner as **12d**. Yield 56%; mp 82 °C; IR (KBr disk) 3024, 1768, 1495, 914 cm^{-1}; ^1H NMR($CDCl_3$) δ = 2.18 (3H, s), 2.23 (3H, s), 3.87 (2H, s), 6.86 (1H, d, J = 2.7 Hz), 6.97 (1H, dd, J = 2.7, 8.6 Hz), 7.05 (1H, d, J = 8.6 Hz), 7.14 (2H, d, J = 7.3 Hz), 7.20 (1H, t, J = 7.3 Hz), 7.27 (2H, t, J = 7.3 Hz); Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%, Found: C, 71.57; H, 5.64%.

2-Heptyl-*p*-phenylene diacetate (12f) was prepared in the same manner as **12d**. Yield 51%; IR (neat) 2927, 1765, 1369, 1211, 1173 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.86 (3H, t, J = 6.9 Hz), 1.25 - 1.30 (8H, m), 1.50 - 1.55 (2H, m), 2.26 (3H, s), 2.29 (3H, s), 2.46 (2H, t, J = 7.9 Hz), 6.91 (1H, dd, J = 2.7, 8.6 Hz), 6.95 (1H, d, J = 2.7 Hz), 6.99 (1H, d, J = 8.6 Hz); Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27%, Found: C, 70.00; H, 8.25%.

Preparation of prenyl and phytyl substituted cyclopropanols 15a and 15b.

6-Methyl-5-hepten-2-yn-1-ol (20a).
i) Alkylation.

To a THF solution (40 mL) of 3-(*t*-butyldimethylsiloxy)-1-propyne (8.49 g, 49.9 mmol) and hexamethylphosphoric triamide (3.3 ml) was added dropwise a hexane solution of *n*-butyllithium (1.6M solution, 31.2 ml, 49.9 mmol) at -78 °C, and the mixture was warmed to -30 °C. After the mixture had been stirred for 30 minutes, 1-bromo-3-methyl-2-butene **17a** (7.44 g, 49.9 mmol) was added dropwise. The mixture was slowly warmed up to rt and was further stirred for 20 hours. Then it was quenched with pH7 phosphate buffer. After the insoluble materials had been filtered off through a pad of Celite, the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography, yielding crude TBS ether of prenyl substituted propargyl alcohol.

ii) Desilylation.

To a methanol solution (20 mL) of the crude TBS ether of prenyl substituted propargyl alcohol was added 10 drops of trimethylsilyl chloride at rt. After being stirred for 1 hour, the reaction mixture was quenched with 20 drops of triethylamine and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography, yielding 6-methyl-5-hepten-2-yn-1-ol (**20a**) in 52% yield; IR (neat) 3336(br), 2920, 1446, 1012 cm^{-1}; ^1H NMR($CDCl_3$) δ = 1.56 (1H, br), 1.61 (3H, s) , 1.69 (3H, s), 2.90 (2H, d, J = 6.9 Hz), 4.23 (2H, s), 5.15 (1H, t, J = 6.9 Hz); HRMS Calcd for $C_8H_{12}O$: 124.0889, Found: 124.0887.

6,10,14,18-Tetramethylnonadec-5-en-2-yn-1-ol (20b) was prepared in the same manner as **20a**. Yield 59%; IR (neat) 3327(br), 2952, 2927, 2868, 1464, 1379 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.82 (3H, d, J = 6.6 Hz), 0.83 (3H, d, J = 6.6 Hz), 0.84 (6H, d, J = 6.7 Hz), 1.03 - 1.38(17H, m), 1.46 - 1.52 (3H, m), 1.59 (3H, s), 1.92 - 1.96 (2H, m), 2.91 (2H, d, J = 6.9 Hz), 4.22 - 4.24 (2H, m), 5.15 (1H, t, J = 6.9 Hz); HRMS Calcd for $C_{23}H_{42}O$: 334.3235, Found: 334.3223.

1-Bromo-6-methyl-5-hepten-2-yne (21a).

To a dichloromethane solution (15 mL) of 6-methyl-5-hepten-2-yn-1-ol (**20a**) (1.24 g, 10.0 mmol) and carbon tetrabromide (4.15 g, 12.5 mmol) was added portionwise triphenylphosphine (3.92 g, 15.0 mmol) at 0 °C. After the mixture had been stirred at 0 °C for 10 minutes, the solvent was removed under reduced pressure. Diethylether was added to the residue and it was filtered off through a pad of Celite and extracted thoroughly with diethyl ether several times. The solvent of the combined filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography, yielding 1-bromo-6-methyl-5-hepten-2-yne (**21a**) in 57% yield; IR (neat) 2976, 1446, 1213, 609, cm^{-1}; ^1H NMR($CDCl_3$) δ = 1.61 (3H, s), 1.69 (3H, s), 2.93 (2H, d, J = 6.9 Hz), 3.91 (2H, t, J = 2.4 Hz), 5.12 - 5.16 (1H, m); HRMS Calcd for $C_8H_{11}Br$: 186.0044, Found: 186.0032.

1-Bromo-6,10,14,18-tetramethylnonadec-5-en-2-yne (21b) was prepared in the same manner as **21a**. Yield 72%; IR (neat) 2952, 2925, 2868, 1462, 1377 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.82 (3H, d, J =6.7 Hz), 0.83 (3H, d, J =6.7 Hz), 0.85 (6H, d, J =6.7 Hz), 1.01 - 1.38 (17H, m), 1.46 - 1.50 (2H, m), 1.59 (3H, s), 1.93 - 1.97 (2H, m), 2.94 (2H, d, J = 6.8 Hz), 3.90 - 3.92 (2H, m), 5.13 (1H, t, J = 6.8 Hz); HRMS Calcd for $C_{23}H_{41}Br$: 396.2392, Found: 396.2394.

1-[1-(3-Methylbut-2-enyl)-1,2-propadienyl]cyclopropanol (15a).

A suspension of powdered aluminum (88 mg, 3.3 mmol) and mercuric chloride (40 mg) in THF (1 mL) was refluxed for 30 minutes. After the mixture was cooled to rt, a THF solution (7 mL) of 1-bromo-6-methyl-5-hepten-2-yne (**21a**) (604 mg, 3.23 mmol) was added dropwise to the suspension and the mixture was refluxed for 1 hour. In another flask, a diethyl ether solution (2.5 mL) of 1-ethoxycyclopropanol (329 mg, 3.23 mmol) was added dropwise to a diethyl ether solution of methylmagnesium iodide (1.7 M solution, 1.9 ml, 3.23 mmol) at 0 °C, and then the mixture was warmed to rt. The above propargyl aluminum reagent was added to the diethyl ether suspension of iodomagnesium salt of cyclopropanol hemiacetal at 0 °C. After the mixture had been stirred at rt overnight, it was quenched with pH7 phosphate buffer and the organic materials were extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography to give 1-[1-(3-methylbut-2-enyl)-1,2-propadienyl]cyclopropanol (**15a**) in 49 % yield; IR (neat) 3325(br), 2916, 1955, 1207, 847 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.72 - 0.74 (2H, m), 0.89 - 0.91 (2H, m), 1.69 (3H, s), 1.70 (3H, s), 2.23 (1H, brs), 2.76 - 2.80 (2H, m), 4.76 (2H, t, J = 3.3 Hz), 5.22 - 5.25 (1H, m); HRMS Calcd for $C_{11}H_{16}O$: 164.1202, Found: 164.1197.

1-[1-(3,7,11,15-Tetramethylhexadec-2-enyl)-1,2-propadienyl]cyclopropanol (15b) was prepared in the same manner as **15a**. Yield 50%; IR (neat) 3400(br), 2954, 2927, 2866, 1955, 1462, 1377 cm^{-1}; ^1H NMR($CDCl_3$) δ = 0.73 - 0.76 (2H, m), 0.82 - 0.85 (12H, m), 0.89 - 0.92 (2H, m), 1.03 - 1.37 (17H, m), 1.48 - 1.52 (2H, m), 1.61 (3H, s), 1.93 - 1.97 (2H, m), 2.08 (1H, brs), 2.78 - 2.80 (2H, m), 4.77 (2H, t, J = 3.3 Hz), 5.23 - 5.26 (1H, m); HRMS Calcd for $C_{26}H_{46}O$: 374.3551, Found: 374.3553.

$Co_2(CO)_8$ promoted transformation of 1-(1,2-propadienyl)cyclopropanols 15a and 15b to hydroquinone derivatives 13a, 13b, 14a and 14b.

2-Methyl-3-(3-methylbut-2-enyl)-*p*-phenylenediacetate (13a).[17]

To an AcOEt solution (18 mL) of $Co_2(CO)_8$ (104 mg, 0.304 mmol) was added dropwise an AcOEt solution (10 mL) of 1-[1-(3-methylbut-2-enyl)-1,2-propadienyl]cyclopropanol (**15a**) (45.8 mg, 0.279 mmol) over 10 minutes at rt. The mixture was stirred overnight, and after disappearance of **15a** was confirmed by TLC, acetic anhydride (1 mL), triethylamine (1 mL) and a catalytic amount of dimethylaminopyridine were added. The mixture was stirred overnight and quenched with pH7 phosphate buffer. Organic materials were

extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified with preparative TLC (hexane : ethyl acetate = 4 : 1) to give 2-methyl-3-(3-methylbut-2-enyl)-*p*-phenylenediacetate(**13a**) in 45% yield; ^{1}H NMR($CDCl_3$) δ = 1.66 (3H, s), 1.72 (3H, s), 2.08 (3H, s), 2.27 (3H, s), 2.29 (3H, s), 3.23 (2H, d, J = 6.7 Hz), 4.96 (1H, t, J = 6.7 Hz), 6.87 (2H, s).

2-Methyl-3-(3,7,11,15-tetramethylhexadec-2-enyl)-*p*-phenylenediacetate (13b) was prepared in the same manner as **13a**.[17] Yield 33%; ^{1}H NMR($CDCl_3$) δ = 0.81 (3H, d, J = 6.6 Hz), 0.82 (3H, d, J = 6.6 Hz), 0.85 (6H, d, J = 6.6 Hz), 1.01 - 1.34 (17H, m), 1.48 - 1.52 (2H, m), 1.70 (3H, s), 1.89 - 1.93 (2H, m), 2.07 (3H, s), 2.27 (3H, s), 2.29 (3H, s), 3.24 (2H, d, J = 6.5 Hz), 4.95 (1H, t, J = 6.5 Hz), 6.87 (2H, s).

2-Methyl-3-(3-methylbut-2-enyl)-*p*-benzoquinone (14a).

To an AcOEt solution (120 mL) of $Co_2(CO)_8$ (997 mg, 2.92 mmol) was added dropwise an AcOEt solution (25 mL) of 1-[1-(3-methylbut-2-enyl)-1,2-propadienyl]cyclopropanol (**15a**) (300 mg, 1.83 mmol) over 10 minutes at rt. The mixture was stirred for about 2 hours and after disappearance of **15a** was confirmed by TLC, triethylamine (8 mL) was added. After 2 hours stirring, a mixture of $FeCl_3$(8.0 g), H_2O(32 ml) and EtOH(16 ml) were added. After being stirred overnight at rt , the mixture was quenched with pH7 phosphate buffer and organic materials were extracted with ethyl acetate. The organic layer was washed successively with 4% aqueous sodium bicarbonate, H_2O and brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified with preparative TLC (hexane : ethyl acetate = 4 : 1) to give 2-methyl-3-(3-methylbut-2-enyl)-*p*-benzoquinone (**14a**) in 45% yield; IR (neat) 2920, 1655, 1304, 833 cm^{-1}; ^{1}H NMR($CDCl_3$) δ = 1.66 (3H, s), 1.73 (3H, s), 2.02 (3H, s), 3.17 (2H, d, J = 6.7 Hz), 4.92 (1H, t, J = 6.7 Hz), 6.69 (2H, s); HRMS Calcd for $C_{12}H_{14}O_2$: 190.0993, Found: 190.0988.

2-Methyl-3-(3,7,11,15-tetramethylhexadec-2-enyl)-*p*-benzoquinone (14b) was prepared in the same manner as **14a**. Yield 34%; IR (neat) 2954, 2924, 2866, 1654, 1460, 1302 cm^{-1}; ^{1}H NMR($CDCl_3$) δ = 0.80 (3H, d, J = 6.4 Hz), 0.82 (3H, d, J = 6.4 Hz), 0.84 (6H, d, J = 6.6 Hz), 0.98 - 1.39 (17H, m), 1.47 - 1.51 (2H, m), 1.71 (3H, s), 1.89 - 1.93 (2H, m), 2.02 (3H, s), 3.19 (2H, d, J = 7.0 Hz), 4.91 (1H, t, J = 7.0 Hz), 6.69 (2H, s); HRMS Calcd for $C_{27}H_{44}O_2$: 400.3341, Found: 400.3323.

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