Synthesis of New 3-(-2-Alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones via Claisen Rearrangement of Original 5-Methoxy-4-(2-propenyloxy)-*o*-benzoquinones

Olivia Reinaud, Patrice Capdevielle, Michel Maumy*

Laboratoire de Recherches Organiques de l'ESPCI, associé au CNRS, 10 rue Vauquelin, F-75231 Paris Cedex 05, France

The Claisen rearrangement is extended to compounds containing the benzoquinone moiety, obtained by regioselective nucleophilic substitution on 4-(*p*-methoxyphenoxy)-5-methoxy-*o*-benzoquinone (**1**). In the most general case, 5-methoxy-4-(2-propenyloxy)-*o*-benzoquinones **3** rearrange quantitatively into (*E*)-3-(2-alkenyl-2-hydroxy-5-methoxy-*p*-benzoquinones **4**. Furfuryl or (2-thienyl)methyl ethers isomerize to 3-(2-methyl-3-furyl)- and 3-(2-methyl-3-thienyl)-2-hydroxy-5-methoxy-*p*-benzoquinones.

This new synthetic method provides an efficient route to new hydroxybenzoquinones closely related to natural compounds. Thus, dihydroardisiaquinone A is synthesized in 5 steps from *p*-methoxyphenol.

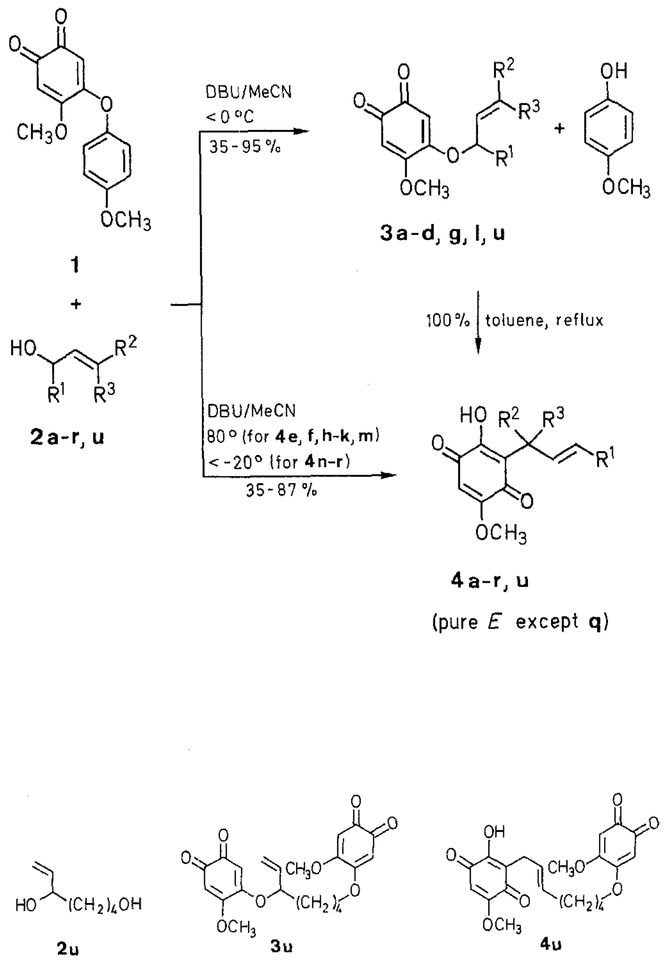
The Claisen reaction is a classical and very useful tool in organic synthesis.[1,2] This rearrangement has been effected on an allyloxy naphthoquinone,[3] but has not previously been extended to the monocyclic benzoquinone series. Indeed allyloxybenzoquinones were until now unknown. We have recently described in a preliminary report[4] that this reaction, applied to an allyloxy-*o*-benzoquinone prepared from the appropriate *o*-benzoquinone **1**, allows the straightforward synthesis of dihydromaesanine (2-hydroxy-5-methoxy-3-pentadecyl-*p*-benzoquinone), a derivative of the natural quinone maesanine.[5] We would like to report here on the extension of this method to a wide variety of allylic alcohols **2**, leading in the first step to the new dialkoxy-*o*-benzoquinones **3**. Regioselective Claisen rearrangement gives 3-(2-alkenyl)-2-hydroxy-5-methoxy-1,4-benzoquinones **4**, which are related to a number of natural products close to maesanine that present interesting biological activities.[6]

Quinonoid compounds (generally *p*- but also some *o*-benzoquinones[7]) bearing potential leaving groups (halides, alkoxy, etc.) undergo well known nucleophilic substitution reactions. Quite uncommon are regioselective displacements of only one group of 4,5-disubstituted *o*-benzoquinones when competition is possible.[8,9] An original dissymmetrically substituted substrate, i.e. with different leaving groups at C-4 and C-5, may allow such a regioselectivity.

Indeed, alkoxy- and aryloxy-*o*-benzoquinones are quite sensitive to nucleophilic reagents. We have previously shown,[4,10-12] that 4-(4-methoxyphenoxy)-5-methoxy-*o*-benzoquinone (**1**), obtained in one step from *p*-methoxyphenol,[4,10] can undergo a selective nucleophilic monosubstitution of the *p*-methoxyphenoxide group by an alcohol in the presence of base. This regioselective reaction is quite general, and we have developed it with allylic alcohols **2**.

High yields (Table 1) of 4-allyloxy-5-methoxy-*o*-benzoquinones **3** are obtained when *o*-benzoquinone **1** and one equivalent of allylic alcohol **2** are reacted in acetonitrile with one equivalent of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in the temperature range of − 40 °C to 0 °C (Scheme **A**). These alcohols are either primary (**2a–c**) or secondary (**2d–r**), with a carbon-chain length varying from C_3 (**2a**) to C_{15} (**2l**). Due to the presence of two reactive sites, diol **2u** gives lower yields, but remains effective reagent. Tertiary alcohols do not provide the corresponding benzoquinones **3**.

The thermal rearrangement of allyloxy-*o*-benzoquinones **3** into (2-alkenyl)-*p*-quinones **4**, according to the Claisen mechanism, proceeds, in general, in quantitative yield with exclusive formation of the *E*-isomer (Scheme **A**, Table 2).



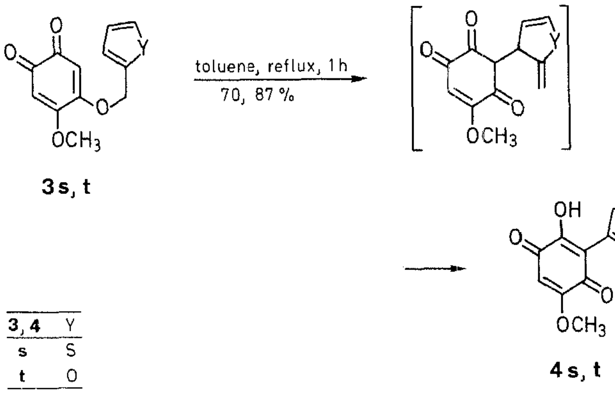
2-4	R^1	R^2	R^3
a	H	H	H
b	H	CH_3	$CH_2CH=C(CH_3)_2$
c	H	C_6H_5	H
d	CH_3	H	H
e	$(CH_2)_2CH_3$	H	H
f	$(CH_2)_3CH_3$	H	H
g	$(CH_2)_4CH_3$	H	H
h	$(CH_2)_2CH=CHCH_3$(*E*)	H	H
i	$(CH_2)_3CH=CH_2$	H	H
j	$(CH_2)_5CH_3$	H	H
k	$(CH_2)_6CH_3$	H	H
l	$(CH_2)_{11}CH_3$	H	H
m	$(CH_2)_4OCH_3$	H	H
n	$CH=CH_2$	$(CH_2)_2CH_3$	H
o	$CH=CH_2$	$CH=CHCH_3$(*E*)	H
p	$(CH_2)_4CH_3$	$CH=CHCH_3$(*E*)	H
q	$C\equiv C(CH_2)_2CH_3$	H	H
r	$(CH_2)_5CH_3$	2-furyl	H

Scheme A

According to the nature of the substituents R^n (n = 1–3), the rate of isomerization is enhanced to the point where the starting material (**3n–r**) is unstable at room temperature (or even below). In some cases, the rearrangement is advantageously carried out on the mixture of *p*-methoxyphenol and *o*-quinone **3e, f, h–k, m** obtained in the substitution reaction. Simultaneous sublimation of the *p*-methoxyphenol is advisable to avoid difficult separation, in which would result in partial decomposition of the relatively unstable *o*-benzoquinones **3**.

The reaction conditions for this quinonic Claisen are quite mild, 5h in refluxing toluene (111 °C) in the less favorable case (**3a** → **4a**), compared with those normally required for aliphatic or aromatic substrates, 150–225 °C.[2] Such a rate acceleration had already been noticed in the rearrangement of propargyloxy-*o*-benzoquinones.[10]

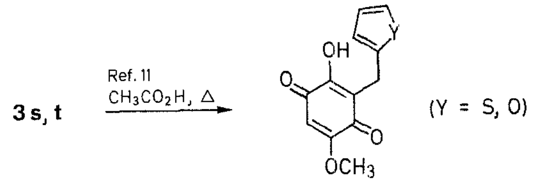
Furfuryloxy- and (2-thienyl)methyloxy-*o*-benzoquinones **3s, t** can be as effective as their allyloxy analogs in this Claisen type reaction, and afford the respective isomers **4s, t** by heating in toluene (Scheme **B**).



3,4	Y
s	S
t	O

Scheme **B**

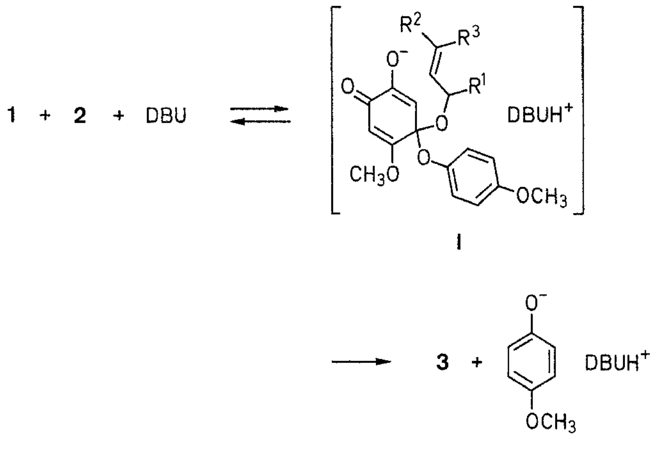
Examples in literature[13] in which these heterocycles undergo allylic rearrangement are uncommon, probably because of the increased activation energy due to loss of aromaticity in the transition state. Besides, in a previous paper[11] we have shown that **3s, t**, when heated in acetic acid, give rise to hydroxy quinones, which are isomers of **4s, t**.



This acid-catalyzed rearrangement does not occur in toluene. On the other hand, with *o*-benzoquinones obtained by substitution of **1** with (1-methyl-2-pyrrolyl)methanol, with a secondary furfurylic alcohol, or with its thiophenic analog, non-Claisen migration of the alkyl group takes place spontaneously during the work-up of the reaction **1** → **3**.[11] Benzyl ethers such as 5-methoxy-4-(1-phenylethoxy)-*o*-benzoquinone[11] are inert in non-acidic medium (4 days in refluxing toluene), which can be explained by the higher aromatic stabilization of benzenic compared with heterocyclic nuclei.[14] Moreover, it is well known that vinyl benzyl ether does not undergo Claisen rearrangement.[15]

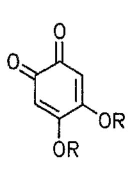
We have also studied the influence of structural parameters in various alcohols **2** on the rate and selectivity of steps **1** + **2** → **3** and **3** → **4**.

According to transesterification studies,[16] it may be considered that the reaction of nucleophilic substitution on *o*-benzoquinone **1** begins with the general base-catalyzed formation of an anionic intermediate **I**, which rapidly evolves to product **3** in agreement with the very different leaving group abilities of *p*-methoxyphenoxide and alkoxides.



The great difference between acidities of their conjugate acids (alcohol 2: pKa = 15; *p*-methoxyphenol: pKa = 10.3)[17] results in the irreversibility of the second step with the expulsion of the salt ($DBUH^+$, *p*-$MeOPhO^-$): alcohols 2 are weakly ionized by DBU ($pK_{BH^+} = 11.5$),[18] but *p*-methoxyphenol completely dissociates, so the reaction is complete without excess alcohol. The regioselectivity of the nucleophilic attack (4-position of **1**) may be explained by the difference in electron-attracting strength between both substituents of the starting *o*-benzoquinone **1**.[19]

In some cases, two by-products are isolated: the double substitution product **6** and 4,5-dimethoxy-*o*-benzoquinone **7** (see experimental part). Their formation can be explained by competitive substitution at the 5-position of either *o*-benzoquinone **1** or **3**, with subsequent nucleophilic attack from the liberated methanol.



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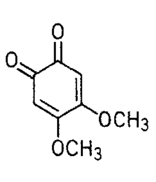

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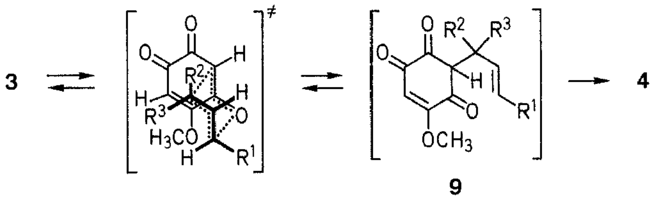
As a rule, the occurrence of these by-products is minimized when nonbulky alcohols **2** are used; thus, a weaker base such as triethylamine may be chosen to achieve nucleophilic substitution by allylic alcohol **2a** and regioselectivity remains quite good (yield = 94%). In the same way, we have previously shown[10] how propargyl alcohols react in presence of triethylamine with complete regioselectivity. With fatty alcohols **2**, the 4-position of the starting material **1** becomes less accessible comparatively to the 5-position, because the *p*-methoxyphenoxy group is much more bulky than the methoxy group.

Allyloxy-*o*-benzoquinones **3** undergo a facile thermal rearrangement to *p*-benzoquinones **4**, according to the same mechanism as that proposed for the Claisen rearrangement of allyl and aryl ethers.[2] A [3,3]-sigmatropic rearrangement of 4-allyloxy-5-methoxy-*o*-benzoquinones **3** provides intermediate cyclohexentriones **9**, which rapidly enolize into the more stable *p*-benzoquinone isomers (rather than the *o*-isomers), i.e. 3-(2-alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones **4**.



As usual,[20] the transition state is represented by a quasi-chair conformation with equatorial R^1 substituent in order to minimize 1,3-diaxial steric interactions between R^1, the quinone moiety and the methoxy group. The stereochemistry of the new double bond (position 2–3 of the chain) is exclusively *trans*, except when R^1 is C≡C. Indeed, the rearrangement of 5-methoxy-4-(1-vinyl-2-hexynyloxy)-*o*-benzoquinone (**3q**) provides an *E*/*Z* ratio of 70 : 30 for *p*-quinones **4q**/**q'**. In the acyclic substrates (vinyl enyn ethers), this loss of stereoselectivity has

Table 1. 5-Methoxy-4-(2-propenyloxy)-*o*-benzoquinones **3** Prepared

Product	Reaction Conditions (Temp., Time)	Yield[a] (%)	mp (°C)	^{1}H-NMR (90 MHz/$CDCl_3$/TMS) δ, *J* (Hz)
3a[b]	−30 °C, 1 h; −20 °C, 0.5 h	95	160	3.78 (s, 3H, OCH_3); 4.55 (d br, 2H, *J* = 5, CH_2); 5.3–5.6 (m, 2H, $=CH_2$); 5.73, 5.75 (2s, $2H_{quin}$); 5.75–6.25 (m, 1H, CH=)
3b[b]	−30 °C, 1 h; −20 °C, 1 h	71	76	1.6, 1.67, 1.83 (3s, 9H, $3CH_3$); 2.1 (m, 4H, $(CH_2)_2$); 3.9 (s, 3H, OCH_3); 4.55 (d br, 2H, *J* = 7, OCH_2); 5.1, 5.48 (2t, 2H, *J* = 7, 2 =CH); 5.75, 5.78 (2s, $2H_{quin}$)
3c[b]	−30 °C, 1 h; −25 °C, 3.5 h	77	152	3.95 (s, 3H, OCH_3); 4.73 (d, 2H, *J* = 6, CH_2); 5.78, 5.83 (2s, $2H_{quin}$); 6.35 (dt, 1H, *J* = 6, 16, $CH_2C\underline{H}=$); 6.78 (d, 1H, *J* = 16, $=C\underline{H}Ph$); 7.4 (s br, $5H_{arom}$)
3d[b]	−10 °C, 2.5 h	90	98	1.5 (d, 3H, *J* = 7, CH_3); 3.88 (s, 3H, OCH_3); 4.8 (q br, 1H, *J* = 7, OCH); 5.17–5.43 (m, 2H, $=CH_2$); 5.55–6.05 (m, 1H, CH=); 5.73 (2s, $2H_{quin}$)
3g	−30 °C, 1 h; −20 °C, 5 h	73	73	0.88 (t br, 3H, CH_3); 1.33 (m, 6H, $(CH_2)_3$); 1.8 (m, 2H, $OCHC\underline{H}_2$); 3.88 (s, 3H, OCH_3); 4.6 (q br, 1H, *J* = 6, OCH); 5.15–5.5 (m, 2H, $=CH_2$); 5.58–5.98 (m, 1H, CH=); 5.70, 5.73 (2s, $2H_{quin}$)
3l[c]	0 °C, 5 h[d]	60	70	0.88 (t br, 3H, CH_3); 1.25 (s br, 2OH, $(CH_2)_{10}$); 1.77 (m, 2H, $OCHC\underline{H}_2$); 3.88 (s, 3H, OCH_3); 4.6 (q br, 1H, *J* = 6, OCH); 5.14–5.4 (m, 2H, $=CH_2$); 5.58–5.98 (m, 1H, CH=); 5.70, 5.73 (2s, $2H_{quin}$)
3u	−20 °C, 6.5 h	45	dec	1.3–2.1 (m, 6H, $(CH_2)_3$); 3.85 (s, 3H, OCH_3); 3.98 (t, 2H, *J* = 6, OCH_2); 4.63 (q br, 2H, *J* = 6, OCH); 5.15–5.45 (m, 2H, $=CH_2$); 5.58–5.98 (m, 1H, CH=); 5.68, 5.72 (2s, $4H_{quin}$)
3v	−20 °C, 10 h[d]	35	dec	1.17 (s br, 16H, $(CH_2)_8$); 1.68 (m, 4H, $2CH_2$); 3.82 (s, 6H, $2OCH_3$); 4.55 (q br, 2H, *J* = 6, 2OCH); 5.1–5.4 (m, 4H, 2 $=CH_2$); 5.5–5.95 (m, 2H, 2CH=); 5.64, 5.67 (2s, $4H_{quin}$)

[a] Yield of isolated products **3** based on **1**.

[b] IR(KBr), ν (cm^{-1}): **3a**: 1665, 1655, 1585 (br), 1250 (br), 1240 (sh), 1230 (sh), 850; **3b**: 1680, 1670, 1660 (sh), 1650 (sh), 1590, 1580, 1255, 1245, 850, 820; **3c**: 1670 (sh), 1655 (br), 1590, 1585, 1255 (br), 845; **3d**: 1670 (br), 1650 (sh), 1590 (br), 1255, 1235, 835.

[c] See Ref. 4.

[d] The reaction is carried out in a 2 : 1 mixture of MeCN/EtCN to insure solubility of alcohol **2**.

Table 2. 3-(2-Alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones **4** Prepared.

Product	Reaction Conditions (Time, Temp.)	Yield[a] (%)	mp (°C)	Molecular[b] Formula	IR ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
4a	5 h refl. toluene	100	100	$C_{10}H_{10}O_4$ (194.2)	3340, 1660, 1635, 1630, 1600, 1590, 1215 (br), 985, 910, 840, 795, 760	(90 MHz): 3.17 (d, 2H, J = 6, CH_2); 3.87 (s, 3H, OCH_3); 4.9–5.2 (m, 2H, =CH_2); 5.6–6.05 (m, 1H, =CH); 5.85 (s, 1H_{quin}); 7.4 (s, 1H, OH)
4b	1 h refl. toluene	100	7	$C_{17}H_{22}O_4$ (290.3)	3300, 1665, 1655 (sh), 1645 (br), 1610, 1605 (sh), 1235, 1225, 1005, 915, 840, 800	(90 MHz): 1.5–1.65 (m: 9H, 3CH_3); 1.6–2.21 (m: 4H, $(CH_2)_2$); 3.87 (s, 3H, OCH_3); 4.8–5.1 (m, 3H, =CH_2, $CH_2C\underline{H}$=); 5.88 (s, 1H_{quin}); 6.23 (dd, 1H, J = 10, 18, CCH =); 7.9 (s, 1H, OH)
4c	0.5 h refl. toluene	100	181	$C_{16}H_{14}O_4$ (270.3)	3310, 1665, 1650, 1615 (sh), 1605, 1495, 1450, 1225 (br), 930, 850, 800, 770, 705	(90 MHz): 3.83 (s, 3H, OCH_3); 5.0–5.25 (m, 2H, =CH_2); 5.83 (s, 1H_{quin}); 6.15–6.8 (m, 1H, =CH); 7.3 (m, 5H_{arom}); 7.45 (s br, 1H, OH)
4d[c]	2 h refl. toluene	100	107	$C_{11}H_{12}O_4$ (208.2)	3350, 1660, 1650, 1595 (br), 1205 (br), 970, 840, 760	(90 MHz): 1.6 (d, 3H, J = 5, CH_3); 3.1 (d, 2H, J = 5, CH_2); 3.87 (s, 3H, OCH_3); 5.4–5.65 (m, 2H, HC=CH); 5.83 (s, 1H_{quin}); 7.25 (s, 1H, OH)
4e	−30°C, 1 h; −20°C, 4 h; 5 h, 80°C/0.3 mbar[d]	(73)	86	$C_{13}H_{16}O_4$ (236.3)	3350, 1660, 1630, 1595 (br), 1200 (br), 960, 840, 795, 760	(90 MHz): 0.83 (t, 3H, J = 6, CH_3); 1.3 (sext, 2H, J = 7, $C\underline{H}_2CH_3$); 1.9 (q br, 2H, J = 7, =$CHC\underline{H}_2$); 3.1 (d br, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.45 (m, 2H, HC =CH); 5.83 (s, 1H_{quin}); 7.3 (s, 1H, OH)
4f[c]	−30°C, 1 h; −20°C, 5 h; 5 h, 80°C/0.3 mbar[d]	(76)	91	$C_{14}H_{18}O_4$ (250.3)	3340, 1660, 1635, 1595 (br), 1210 (br), 970, 840, 760	(90 MHz: 0.83 (t br, 3H, J = 6, CH_3); 1.25 (m, 4H, $(CH_2)_2$); 1.9 (q br, 2H, J = 6, =$CHC\underline{H}_2$); 3.1 (d br, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.45 (m, 2H, HC =CH); 5.83 (s, 1H_{quin}); 7.25 (s, 1H, OH)
4g[c]	1 h refl. toluene	100	105	$C_{15}H_{20}O_4$ (264.3)	3340, 1660, 1635, 1595 (br), 1210 (br), 970, 840, 760	(90 MHz): 0.83 (t br, 3H, J = 6, CH_3); 1.25 (m, 6H, $(CH_2)_3$); 1.9 (q br, 2H, J = 6, =$CHC\underline{H}_2$); 3.1 (d br, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.45 (m, 2H, HC =CH); 5.83 (s. 1H_{quin}); 7.3 (s, 1H, OH)
4h	−30°C, 1 h; −20°C, 5 h; 5 h, 80°C/0.3 mbar[d]	(75)	98	$C_{15}H_{18}O_4$ (262.3)	3340, 1660, 1635, 1595 (br), 1205 (br), 965 (br), 840, 760	(90 MHz): 1.6 (d, 3H, J = 3, CH_3); 2.0 (s br, 4H, $(CH_2)_2$); 3.12 (d, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.43 (m, 4H, 4 =CH); 5.85 (s, 1H_{quin}); 7.37 (s, 1H, OH)
4i[c]	−30°C, 1 h; −20°C, 5 h; 5 h, 80°C/0.3 mbar[d]	(66)	80	$C_{15}H_{18}O_4$ (262.3)	3340, 1660, 1635, 1630, 1605, 1590, 1205 (br), 970, 910, 840, 800, 760	(90 MHz): 1.47 (m, 2H, $CH_2C\underline{H}_2CH_2$); 1.95 (m, 4H, $C\underline{H}_2CH_2C\underline{H}_2$); 3.12 (d, 2H, J = 6, =CCH_2); 3.87 (s, 3H, OCH_3); 4.7–5.1 (m, 2H, =CH_2); 5.48 (m, 2H, HC=CH); 5.6–6.0 (m, 1H, $C\underline{H}$=CH_2); 5.83 (s, 1H_{quin}); 7.3 (s, 1H, OH)
4j[c,e]	−30°C, 1 h; −20°C, 5 h; 5 h, 80°C/0.3 mbar[d]	(65)	95	$C_{16}H_{22}O_4$ (278.3)	3345, 1660, 1635, 1595 (br), 1210 (br), 970, 840, 805, 760	(90 MHz): 0.87 (s br, 3H, J = 6, CH_3); 1.25 (s br, 8H, $(CH_2)_4$); 1.9 (q br, 2H, J = 6, =$CHC\underline{H}_2$); 3.1 (d br, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.45 (m, 2H, HC =CH); 5.83 (s, 1H_{quin}); 7.3 (s, 1H, OH)
4k	−30°C, 1 h; −20°C, 5 h; 5 h, 80°C/0.3 mbar[d]	(60)	101	$C_{17}H_{24}O_4$ (292.4)	3350, 1660, 1635, 1595 (br), 1205, 960, 840, 760	(90 MHz): 0.87 (t br, 3H, J = 6, CH_3); 1.25 (s br, 10H, $(CH_2)_5$); 1.9 (q br, 2H, J = 6, =$CHC\underline{H}_2$); 3.1 (d br, 2H, J = 5, =CCH_2); 3.87 (s, 3H, OCH_3); 5.45 (m, 2H, HC =CH); 5.83 (s, 1H_{quin}); 7.3 (s, 1H, OH)
4l[c,f]	0.5 h refl. toluene	100	94.5	$C_{22}H_{32}O_4$ (360.5)	3350, 1660, 1635, 1595 (br), 1205, 960, 840, 760	(200 MHz): 0.88 (t br, 3H, J = 6.4, CH_3); 1.24 (s br, 20H, $(CH_2)_{10}$); 1.94 (q br, 2H, J = 6.3, =$CHC\underline{H}_2$); 3.13 (dd, 2H, J = 6.2, 1, =CCH_2); 3.86 (s, 3H, CH_3); 5.3–5.6 (m, 2H, J_{AB} = 15.2, HC=CH); 5.85 (s, 1H_{quin}); 7.28 (s, 1H, OH)
4m[e]	−35°C, 2.5 h; −20°C, 4 h; 5 h, 80°C/0.3 mbar[d]	(45)	129	$C_{15}H_{20}O_5$ (280.3)	3400 (br), 1660, 1645, 1600, 1200 (br), 965, 850, 795	(90 MHz): 1.45 (m, 4H, $(CH_2)_2$); 1.95 (q br, 2H, J = 5, =CCH_2); 3.30 (s, 3H, $CH_2OC\underline{H}_3$); 3.33 (t, 2H, J = 7, $C\underline{H}_2OCH_3$); 3.87 (s, 3H, OCH_3); 5.47 (m, 2H, HC =CH); 5.73 (s, 1H_{quin}); 7.45 (s, 1H, OH)
4n	−30°C, 2 h; −20°C, 2 h; spontaneous[g]	(70)[h]	128	$C_{15}H_{18}O_4$ (262.3)	3315, 1655, 1640, 1595, 1215, 955, 900, 845, 800, 760	(90 MHz): 0.87 (t, 3H, J = 6, CH_3); 1.05–1.45 (m, 2H, $C\underline{H}_2CH_3$); 1.55–1.75 (q, 2H, J = 8, $CHC\underline{H}_2$); 3.5–3.8 (m, 1H, CH); 3.87 (s, 3H, OCH_3); 4.9–5.2 (m, 2H, =CH_2); 5.83 (s, 1H_{quin}); 5.9–6.4 (m, 3H, 3 =CH); 7.45 (s, 1H, OH)
4o[e]	−30°C, 2 h; −20°C, 2 h; spontaneous[g]	(35)[h]	133	$C_{15}H_{18}O_4$ (260.3)	3320, 1660, 1640, 1595, 1215, 970, 900, 845, 800, 760	(250 MHz): 1.66 (dd, 3H, J = 6, 1.2, CH_3); 3.87 (s, 3H, OCH_3); 4.34 (t, H_0, J = 7.5); 5.01 (dd, H_g, J = 10, 1.5); 5.13 (dd, H_f, J = 16.8, 1.5); 5.57 (dq, H_a, J = 15.2, 6); 5.76 (ddq: H_b, J = 15.2, 7.5, 1.2); 5.85 (s, 1H_{quin}); 5.98 (dd, H_c, J = 15.1, 7.5); 6.13 (dd, H_d, J = 15.1, 10); 6.31 (td, H_e, J = 10, 16.8); 7.49 (s, 1H, OH)
4p[e]	−30°C, 2 h; −20°C, 2 h; spontaneous[g]	(71)	83	$C_{18}H_{24}O_4$ (304.4)	3315, 1665, 1645, 1600, 1215, 975 (br), 845, 800, 760	(90 MHz): 0.87 (t br, 3H, J = 6, $CH_2C\underline{H}_3$); 1.25 (s br, 6H, $(CH_2)_3$); 1.63 (d, 3H, J = 6, =$CHC\underline{H}_3$); 3.87 (s, 3H, OCH_3); 4.25 (t, 1H, J = 6, CH); 5.2–5.9 (m, 4H, 4 =CH); 5.83 (s, 1H_{quin}); 7.37 (s, 1H, OH)
4q	−30°C, 2 h; −20°C, 2 h; spontaneous[g]	(76)[h]	115 and 128	$C_{15}H_{16}O_4$ (260.3)	3315, 2205, 1655, 1640, 1595, 1215, 960, 845, 795, 760	(250 MHz): 0.96 (t, 3H, J = 7, CH_3); 1.51 (sext, 2H, J = 7, $C\underline{H}_2CH_3$); 2.24 (td, 2H, J = 7, 2.1, ≡CCH_2); 3.22 (dd, 2H, J = 7, 1.4, =CCH_2); 3.87 (s, 3H, OCH_3); 5.58 (dm, 1H, J = 15.7, ≡CCH); 5.86 (s, 1H_{quin}); 6.02 (td, 1H, J = 7, 15.7, $CH_2C\underline{H}$=); 7.5 (s, 1H, OH)

4r	−40 °C, 2 h; −30 °C, 2 h; −20 °C, 2.5 h; spontaneous[g]	(84)	84	$C_{20}H_{24}O_4$ (344.4)	3315, 1660 (sh), 1645, 1600, 1220, 975 (br), 850, 800, 765, 730	(90 MHz): 0.87 (t br, 3H, $J = 6$, CH_3); 1.3 (s br, 8H, $(CH_2)_4$); 2.03 (q br, 2H, $J = 6$, $=CHC\underline{H}_2$); 3.83 (s, 3H, OCH_3); 4.95 (d, 1H, $J = 7$, CH); 5.5–6.0 (m, 2H, HC=CH); 5.87 (s, $1H_{quin}$); 6.1, 6.25 (2m, $2H_{furan}$); 7.25 (s br, $1H_{furan}$); 7.55 (s br, 1H, OH)
4s	1 h refl. toluene	87	190	$C_{12}H_{10}O_4S$ (250.3)	3340, 1665, 1650, 1640, 1605 (br), 1210, 850, 800, 760	(90 MHz): 2.20 (s, 3H, CH_3); 3.90 (s, 3H, OCH_3); 5.95 (s, $1H_{quin}$); 6.85, 7.10 (2d, $2H_{thioph}$, $J = 6$); 7.55 (s br, 1H, OH)
4t[c,e]	1 h refl. toluene	70	148	$C_{12}H_{10}O_5$ (234.2)	3330, 1665, 1640, 1605, 1590, 1210, 845, 795, 760, 730	(90 MHz): 2.23 (s, 3H, CH_3); 3.90 (s, 3H, OCH_3); 5.95 (s, $1H_{quin}$); 6.45, 7.35 (2d, $2H_{furan}$); 7.6 (s br, 1H, OH)
4u	1 h refl. toluene	100	164	$C_{21}H_{22}O_8$ (402.4)	3420 (br), 1665 (sh), 1655 (sh), 1645, 1600, 1585, 1250, 1215, 975, 855, 835 (br), 800	(250 MHz): 1.5, 1.73 (2q, 4H, $J = 7$, $(CH_2)_2$); 2.06 (q, 2H, $J = 7$, $=CHC\underline{H}_2$); 3.14 (d, 2H, $J = 5$, $=CCH_2$); 3.86, 3.89 (2s, 6H, $2OCH_3$); 3.98 (t, 2H, $J = 7$, OCH_2); 5.50 (m, 2H, $J_{AB} = 15.3$, CH=CH); 5.72, 5.76 (2s, $2H_{o\text{-}quin}$); 5.87 (s, $1H_{p\text{-}quin}$); 7.42 (s, 1H, OH)
4v[e]	0.5 h refl. toluene	100	169	$C_{30}H_{38}O_8$ (526.6)	3340, 1660, 1640, 1595 (br), 1210 (br), 970, 840, 760	(200 MHz): 1.22 (s br: 24H, $(CH_2)_{12}$); 1.94 (q br, 4H, $J = 7$, 2 $=CHC\underline{H}_2$); 3.87 (s, 5H, $2OCH_3$); 5.47 (s, 4H, 2CH=CH); 5.84 (s, $2H_{quin}$); 7.28 (s, 2H, 2OH)

[a] Yield of isolated pure **4** from **3**. When corresponding to the 2 successive steps (**1** → **4**), yields are shown in parenthesis.

[b] Satisfactory microanalyses obtained: C ±0.30, except **4o** (−0.40) and **4p**, **r** (−0.42); H ±0.21, S −0.06.

[c] MS: m/z = **4d**: 208, 193, 168, 153, 138, 69; **4f**: 250, 193, 168, 153, 139, 69; **4g**: 264, 193, 168, 153, 139, 69; **4i**: 262, 193, 168, 153, 139, 69; **4j**: 278, 193, 168, 153, 139, 69; **4l**: 262, 193, 168, 153, 139, 69; **4s**: 236, 234, 206, 191, 163, 135, 69.

[d] Realized on mixture **4** and *p*-methoxyphenol.

[e] UV: λ_{max} (nm, log ε) = **4j**: 288 (4.3), 414 (2.7); **4m**: 288 (4.3), 414 (2.7); **4o**: 244 (4.3), 288 (4.4), 418 (2.85); **4p**: 288 (4.3), 418 (2.8); **4s**: 254 (4.0), 290 (4.2), 348 (2.8), 484 (3.0); **4v**: 288 (4.6), 414 (3.0).

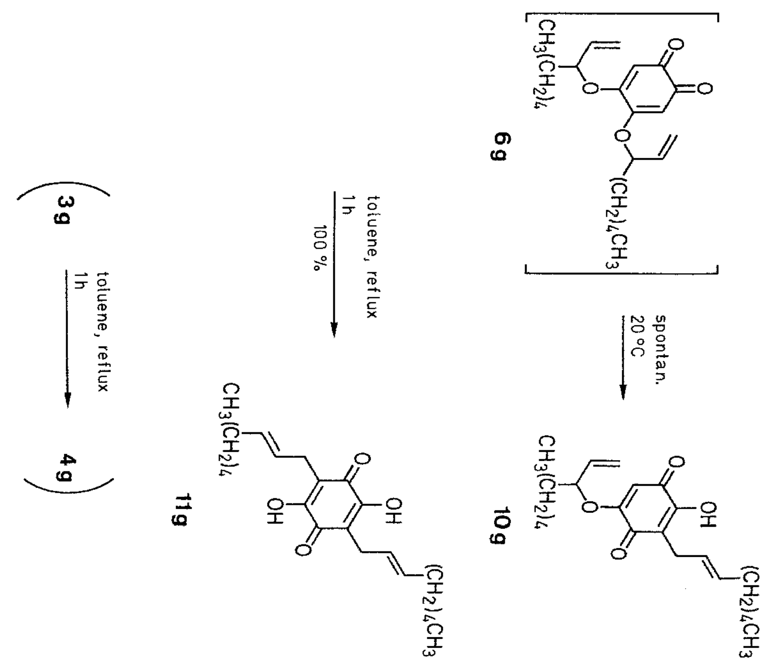
[f] See Ref. 4.

[g] During treatment of reaction **1** → **3**.

[h] The yield corresponds to a mixture of isomers **4**,**4′**.

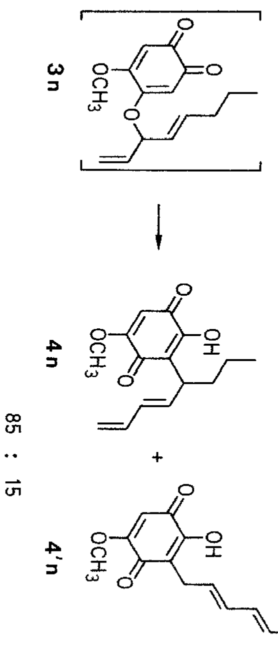
frequently been observed,[21] and can be explained by the less important steric hindrance of a C≡C group in comparison with an alkyl or vinyl one.

In the case of bulky R^1 groups, the rearrangement takes place more quickly (Table 2), because of the steric decompression in the transition state. Such a rate enhancement caused by a bulky R^1 group was also observed in vinyl *o*-substituted aryl ethers.[22] When a bulky group such as 1-pentyl-2-propenyloxy replaces the methoxy group at the 5-position of the quinone substrate, the corresponding *o*-benzoquinone **6** (by-product of the quinone **3** synthesis) spontaneously rearranges to hydroxy quinone **10**. The second Claisen reaction (**10** → **11**) takes place much more slowly.



6g **10g** **11g** **3g** **4g**

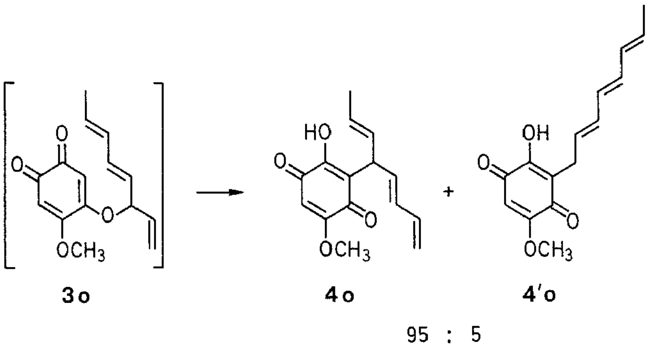
R^2 or R^3 substituents on the allylic double bond induce rate acceleration by transition state stabilization. Unlike R^1, the substituents R^2 and R^3 exhibit unfavorable steric interactions. However, intramolecular competition studies clearly indicate the primacy of the stabilization effect. Thus the rearrangement of 5-methoxy-4-(1-vinyl-2-hexenyloxy)-*o*-benzoquinone (**3n**) preferentially involves the most substituted vinylic bond.



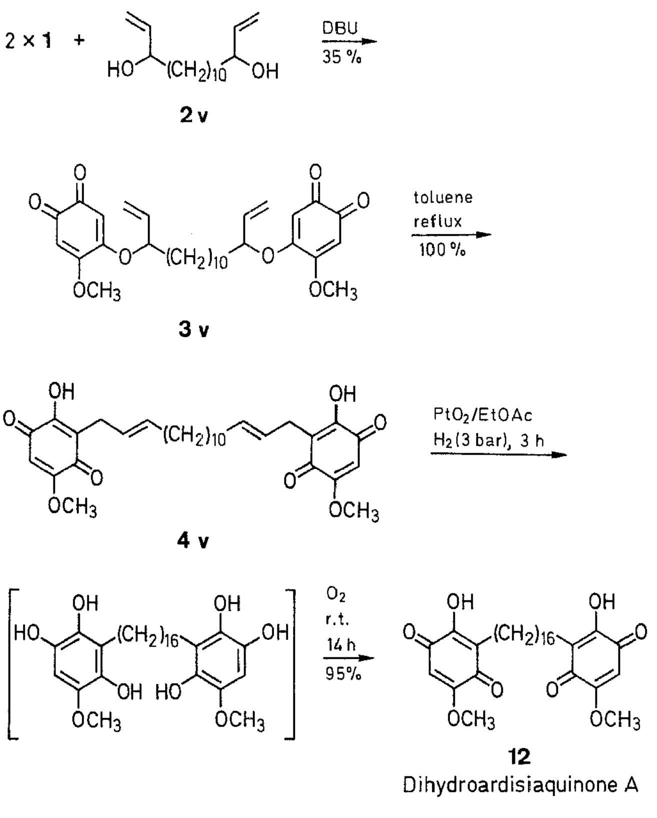
3n **4n** **4′n**

85 : 15

When R^2 is a vinylic group and R^1 is vinyl, the stabilizing effect of R^2 is even clearer.



Furthermore, when either the R^1 or R^2 group is unsaturated, a dramatic rate enhancement is observed: *o*-benzoquinones **3o–r** rearrange even from $-20\,^\circ$C. Moreover, this new Claisen rearrangement of allyloxy-*o*-benzoquinones can be advantageously used to insert a quaternary substituent on the benzoquinone ring (cf. example **4b**).



Finally, to illustrate the great synthetic potential of this new method, we have readily prepared the dihydro derivative of a naturally occurring compound, ardisiaquinone A.[5] The synthesis of this bisquinonyl structure has only been reported once, in a 15-step procedure.[23] According to our method, 1,15-hexadecadien-3,14-diol (**3v**) reacts with two equivalents of quinone **1** to provide, as described above, a symmetrical *p*-quinone **4v**. A catalytic hydrogenation followed by air oxidation affords dihydroardisiaquinone A in very good yield.

Most reagents are commercially available. MeCN was distilled twice from P_4O_{10} and kept under nitrogen over molecular sieves (3 Å). Melting points were taken on a Kofler apparatus, except **4b**, for which a capillary melting point tube was used. IR spectra were recorded on a Perkin-Elmer 298 IR spectrophotometer (KBr; except **4b**: NaCl). UV absorptions were measured on a Hewlett-Packard 8451 A UV spectrophotometer in $CHCl_3$. ^{1}H-NMR spectra were obtained on Varian EM-390 (90 MHz); Bruker AM-200 SY (200 MHz) and AM-250 (250 MHz) spectrometers. The ^{13}C-NMR spectrum was obtained on a Bruker AM-250 spectrometer (62.9 MHz).

The syntheses of *o*-benzoquinones **1**,[10] **3s** and **3t**[11] have been previously described.

Allylic Alcohols 2:

The alcohols **2h**,[24] **2i**,[25] **2j–l**,[26] **2n**,[27] **2o**,[28] **2q**,[29] and **2u**[30] are obtained by classical Grignard reaction. The alcohols **2m**, **2p**, **2r** and **2v** are synthesized by Grignard reaction between acrolein and 4-methoxy-1-bromobutane,[31] (*E,E*)-2,4-hexadienal and 1-bromopentane, 3-(2-furyl)acrolein and 1-bromohexane, and acrolein and 1,10-dibromodecane, respectively.

2m: bp 106–108 °C/12 mbar.

$C_8H_{16}O_2$	calc.	C 66.63	H 11.18
(144.2)	found	66.11	11.27

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 1.2-1.7$ (m, 6 H, $(CH_2)_3$); 2.1 (s, 1 H, OH); 3.33 (s, 3 H, OCH_3); 3.37 (t, 2 H, $J = 6$ Hz, $C\underline{H}_2OCH_3$); 4.05 (q, 1 H, $J = 6$ Hz, CHO); 5.0–5.3 (m, 2 H, $=CH_2$); 5.65–6.05 (m, 1 H, =CH).

2p: bp 125–128 °C/18 mbar.

$C_{11}H_{20}O$	calc.	C 78.51	H 11.98
(168.3)	found	78.86	11.86

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 0.87$ (t, 3 H, $J = 6$ Hz, CH_3); 1.1–1.6 (m, 8 H, $(CH_2)_4$); 1.73 (d, 3 H, $J = 7$ Hz, $=CHC\underline{H}_3$); 2.23 (s, 1 H, OH); 4.05 (q, 1 H, $J = 7$ Hz, CHO); 5.2–6.5 (m, 4 H, 4 =CH).

2r: bp 119–120 °C/0.3 mbar.

$C_{13}H_{20}O_2$	calc.	C 74.96	H 9.68
(208.3)	found	75.21	9.65

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 0.87$ (t, 3 H, $J = 6$ Hz, CH_3); 1.1–1.6 (m, 10 H, $(CH_2)_5$); 2.3 (s, 1 H, OH); 4.2 (q, 1 H, $J = 6$ Hz, CHO); 6.0–6.55 (m, 4 H, 2 =CH and 2 H_{furan}); 7.32 (m, 1 H_{furan}).

2v: mp 49 °C

$C_{16}H_{30}O_2$	calc.	C 75.53	H 11.89
(254.4)	found	75.65	11.95

^{1}H-NMR (250 MHz, $CDCl_3$/TMS): $\delta = 1.28$ (s br, 16 H, $(CH_2)_8$); 1.53 (q, 4 H, $J = 6.3$ Hz, 2 $HCOC\underline{H}_2$); 1.68 (s, 2 H, 2 OH); 4.09 (qdd, 2 H, $J = 6.3$, 1.3, 1.1 Hz, 2 CHO); 5.10 (ddd, 2 H, $J = 10{,}4$, 1.5, 1.1 Hz, 2 $=C\underline{H}(Z)H(E)$; 5.21 (ddd, 2 H, $J = 16.8$, 1.5, 1.3 Hz, 2 $=CH(Z)\underline{H}(E)$); 5.87 (ddd: 2 H, $J = 16.8$, 10.4, 6.3 Hz, 2 =CH).

4-Allyloxy-5-methoxy-*o*-benzoquinone (3a):

Method A: DBU (0.17 ml, 1.15 mmol) is added to a stirred mixture of 5-methoxy-4-(4-methoxyphenoxy)-*o*-benzoquinone (**1**, 300 mg, 1.15 mmol) and allyl alcohol (**2a**; 0.09 mL, 1.32 mmol) at $-30\,^\circ$C in dry MeCN under nitrogen. After 1 h, the temperature is raised to $-20\,^\circ$C. After 30 min more, the starting materials have completely reacted, and a first crop (90 mg) of benzoquinone **3a** is isolated by filtration of the crude mixture and washed with ether (2 × 3 mL). The mother liquor is poured on an alumina column (pH 6, air deactivated) and is quickly eluted with EtOAc. The filtrate is concentrated under reduced pressure and flash chromatography on silica gel (cyclohexane/EtOAc, 50:50, as eluent) gives additional **3a** (122 mg); total yield: 212 mg (95 %).

Method B: To a stirred solution of **1** (300 mg, 1.15 mmol) and **2a** (0.09 mL, 1.32 mmol) in dry MeCN (2 mL) at 20 °C under nitrogen, Et_3N (0.15 mL, 1.15 mmol) is added. After 3.5 h, the brownish solution is concentrated under vacuum, and the orange oil is chromatographed on silica gel (cyclohexane/EtOAc, from 70:30 to 50:50, as eluent) to afford **3a**; yield: 210 mg (94 %).

5-Methoxy-4-(3-phenyl-2-propenyloxy)-*o*-benzoquinone (3c):

To a stirred suspension of **1** (500 mg, 1.9 mmol) and 3-phenyl-2-propen-1-ol (**2c**; 280 mg, 2.1 mmol) in dry MeCN (5 mL) at $-30\,^\circ$C under nitrogen, DBU (0.30 mL, 1.9 mmol) is added in 5 min. After 1 h, some benzoquinone **3c** has precipitated and the temperature is raised to $-25\,^\circ$C. After 1 h more, the starting benzoquinone **1** has completely reacted, and the yellow crystals of **3c** are isolated by suction and washed with EtOAc (2 × 15 mL). The remaining reaction solution is quickly filtered through an alumina column (pH 6, air deactivated), and concentrated under reduced pressure to give a second crop of **3c**; total yield: 400 mg (77 %).

5-Methoxy-4-(1-pentyl-2-propenyloxy)-*o*-benzoquinone (3g); Typical Procedure:

To a stirred suspension of **1** (500 mg, 1.9 mmol) and 1-octen-3-ol (**2g**, 0.32 mL, 2.1 mmol) in dry MeCN (5 mL) at $-30\,^\circ$C under nitrogen, DBU (0.30 mL, 1.9 mmol) is added in 5 min. The mixture becomes brown and homogeneous after 1 h, and the temperature is raised to – 20 °C. After 5 h, quinone **1** has completely reacted; the solution is then poured on an alumina column (pH 6, air deactivated) and the product is quickly eluted with EtOAc. The filtrate is concentrated under reduced pressure, and a flash chromatography on silica gel (cyclohexane/EtOAc, from 0:100 to 50:50, as eluent) affords benzoquinone **3g** as orange-yellow crystals after recrystallization from hexane/ether; yield: 365 mg (73 %).

The first colored fractions afford *2-hydroxy-5-(1-pentyl-2-propenyloxy)-3-(2-octenyl)-p-benzoquinone* (**10g**); yield: 55 mg (8 %); the last ones lead to *4,5-dimethoxy-o-benzoquinone* (**7**); yield: 26 mg (8 %).

The same procedure, in the case of **3d**, affords 2 % of benzoquinone **7**.

10g: ^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 0.87$ (t br, 6 H, $J = 6$ Hz, 2 CH_3); 1.2–2.0 (m, 12 H, 2 $(CH_2)_3$); 3.1 (d, 2 H, $J = 6$ Hz, $=CHC\underline{H}_2$); 4.5 (q, 1 H, $J = 6$ Hz, OCH); 5–6 (m, 5 H, 5 =CH); 5.8 (s, 1 H_{quin}); 6.5–7.5 (s br, 1 H, OH).

7: mp 225 °C (Lit.[8] mp 225–227 °C).

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 3.90$ (s, 6 H, 2 OCH_3); 5.77 (s, 2 H_{quin}).

3-(2-Alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones 4a–d, g, l, u, v; General Procedure:

A solution of *o*-benzoquinone **3** (100 mg) in toluene (10 mL) is heated at reflux until the starting quinone **3** has complectely reacted (TLC). The solvent is then removed under vacuum and pure *p*-quinone **4** is obtained; yield: 100 mg (100 %).

3-(2-Alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones 4e, f, h–k, m; General Procedure:

DBU (0.30 mL, 1.9 mmol) is added within 5 min to a stirred suspension of 5-methoxy-4-(4-methoxyphenoxy)-*o*-benzoquinone (**1**; 500 mg, 1.9 mmol) and alcohol **2** (2.1 mmol) in dry MeCN (5 mL) under nitrogen at the appropriate temperature (see Table 1). After the indicated time (Table 1), the temperature is raised to – 20 °C. When the starting *o*-quinone has completely reacted (TLC), the dark solution is poured on an alumina column (pH 6, air deactivated) and the product is eluted with EtOAc. The filtrate is concentrated under vacuum and a flash chromatography on silica gel (cyclohexane/EtOAc, 70:30, as eluent) affords an orange mixture of *o*-benzoquinone **3** and *p*-methoxyphenol, which is then heated at reduced pressure (0.3 mbar) for 5 h. The crude product (free of *p*-methoxyphenol, which has sublimed) is taken up in CH_2Cl_2 and filtered through silica gel. Pure hydroxy-*p*-benzoquinone **4** is obtained by recrystallization from hexane/ether.

3-(2-Alkenyl)-2-hydroxy-5-methoxy-*p*-benzoquinones 4n–r; General Procedure:

DBU (0.30 mL, 1.9 mmol) is added over 5 min to a stirred suspension of **1** (500 mg, 1.9 mmol) and alcohol **2** (2.1 mmol) in dry MeCN (5 mL) at – 30 °C under nitrogen. The mixture is maintained with stirring at the appropriate temperature (see Table 2) until the starting *o*-benzoquinone **1** has completely reacted (TLC). A dry 0.1 M ether solution of *p*-toluenesulfonic acid is then slowly added to the red mixture, still at low temperature, until it becomes orange (ca. 19 mL). The solution is then poured onto a refrigerated column containing alumina (pH 6, air deactivated, h = 3 cm, at the bottom) and silica gel (h = 0.5 cm, at the top) and the product is quickly eluted with EtOAc/AcOH (98:2). The filtrate is concentrated under reduced pressure and a flash chromatography on silica gel (cyclohexane/EtOAc/AcOH, from 100:0:0 to 50:50:2, as eluent) provides a mixture of benzoquinone **4** and *p*-methoxyphenol, which is then heated under reduced pressure (0.3 mbar) at 80 °C until all *p*-methoxyphenol sublimes. The crystalline crude product is taken up in CH_2Cl_2, filtered through silica gel, and concentrated under reduced pressure. Pure *p*-benzoquinone **4** is obtained after recrystallization from hexane/ether.

Relative determination of isomers **4n′**, **o′**, **q′** simultaneously formed with quinones **4n**, **o**, **q** is given by ^{1}H-NMR spectra of the crude products (**4n**/**4n′** = 85:15; **4o**/**4o′** = 95:5; **4q**/**4q′** = 70:30).

2-Hydroxy-5-methoxy-3-[(E,E)-2,4-octadienyl]-p-benzoquinone (**4n′**):
^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 3.17$ (d, 2 H, $J = 6$ Hz, $=CCH_2$).

2-Hydroxy-5-methoxy-3-[(E,E,E)-2,4,6-octatrienyl]-p-benzoquinone (**4o′**):
^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 3.73$ (d, 2 H, $J = 6$ Hz, $=CCH_2$).

2-Hydroxy-5-methoxy-3-[(Z)-2-octen-4-ynyl]-p-benzoquinone (**4q′**):
^{1}H-NMR (250 MHz, $CDCl_3$/TMS): $\delta = 1.02$ (t, 3 H, $J = 7$ Hz, CH_3); 1.51 (s, 2 H, $J = 7$ Hz, $C\underline{H}_2CH_3$); 2.24 (td, 2 H, $J = 7$, 2.1 Hz, CCH_2); 3.22 (dd, 2 H, $J = 7$, 1.4 Hz, $=CHC\underline{H}_2$); 3.87 (s, 3 H, OCH_3), 5.51 (dm, 1 H, $J = 10.5$ Hz, CCH=); 5.81 (td, 1 H, $J = 7$, 10.5 Hz, $CH_2C\underline{H}=$); 5.87 (s, 1 H_{quin}); 7.5 (s, 1 H, OH).

Regioisomers **4n**, **n′** and **4o**, **o′** are not separable but *p*-benzoquinone **4q** can be obtained free of its stereoisomer **4q′** by further recrystallizations from hexane/ether.

3-Substituted 2-Hydroxy-5-methoxy-*p*-benzoquinones 4s, t; General Procedure:

A solution of *o*-benzoquinone **3** (100 mg) in toluene (20 mL) is heated at reflux until starting quinone **3** has completely reacted. The solution is then concentrated under vacuum; a flash chromatography on silica gel (cyclohexane/EtOAc/AcOH, 20:80:1, as eluent) and further recrystallization from hexane/ether affords pure *p*-benzoquinones **4s**, **t** as red crystals.

2,5-Dihydroxy-3,6-bis(2-octenyl)-*p*-benzoquinone (11g):

A solution of 2-hydroxy-5-(1-pentyl-2-propenyloxy)-3-(2-octenyl)-*p*-benzoquinone (**10g**, 100 mg, 0.28 mmol) in toluene (10 mL) is heated at reflux for 1 h. The solvent is then removed under reduced pressure and pure benzoquinone **11g** is obtained as orange crystals; yield: 100 mg (100 %); mp 148 °C.

$C_{22}H_{32}O_4$	calc.	C 73.30	H 8.95
(360.5)	found	73.04	8.92

IR: $\nu = 3320$, 1640, 1610 (br), 1205, 1190, 970, 765 cm^{-1}.

UV: λ_{max} (log ε) = 294 (4.35), 412 nm (2.35).

^{1}H-NMR (90 MHz, $CDCl_3$/TMS): $\delta = 0.87$ (t br, 6 H, $J = 6$ Hz, 2 CH_3); 1.28 (m, 12 H, 2 $(CH_2)_3$); 1.97 (q br, 4 H, $J = 6$ Hz, 2 $=CHC\underline{H}_2$); 3.12 (d, 4 H, $J = 6$ Hz, 2 $=CCH_2$); 5.48 (m, 4 H, 2 HC=CH); 7.5 (s br, 2 H, 2 OH).

Dihydroardisiaquinone A (12):

A suspension of hydroxyquinone **4v** (526 mg, 1 mmol) and PtO_2 (11 mg, 0.05 mmol) in EtOAc (60 mL) is stirred for 3 h under hydrogen at a pressure of 3 bar in a glass-coated pressure reactor. The colorless mixture is then stirred under air for 14 h. The partially precipitated new quinone is dissolved in additional EtOAc, filtered through silica gel, and concentrated (10 mL) to afford pale, lemon-yellow crystals of **12** (380 mg), which are isolated by vacuum filtration and washed with ether (2 × 10 mL). The mother liquor is concentrated again and a second crop of **12** (120 mg) is obtained; total yield: 500 mg (95 %); mp 172 °C (Lit.[5] mp 174–176 °C).

$C_{30}H_{42}O_8$	calc.	C 67.90	H 7.98
(530.6)	found	68.11	8.09

IR: $\nu = 3340$, 1660, 1655 (br), 1635, 1600 (br), 1215, 1205, 920, 800, 760 cm^{-1}.

MS (70 eV): $m/z = 532$, 530, 502, 193, 169, 168, 167, 153, 139, 69.

^{1}H-NMR (250 MHz, $CDCl_3$/TMS): $\delta = 2.25$ (s br, 24 H, $(CH_2)_{12}$); 1.45 (m, 2 $=CCH_2C\underline{H}_2$); 2.43 (t, 4 H, $J = 7$ Hz, 2 $=CCH_2$); 3.87 (s, 6 H, 2 OCH_3); 5.85 (s, 2 H_{quin}); 7.25 (s, 2 H, 2 OH).

^{13}C-NMR ($CDCl_3$/TMS): $\delta = 22.7$, 28.1, 29.4, 29.6, 29.7 (5t, $(CH_2)_8$); 56.7 (q, 2 OCH_3); 102.2 (d, 2 =CH); 119.4 (s, 2 =C); 151.6, 161.3 (2s, 4 =CO); 181.7, 182.9 (2s, 4 C=O).

Received: 14 September 1987; revised: 19 November 1987

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