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Allylation of quinones by allylic indium reagents

Shuki Araki, Nobuhito Katsumura and Yasuo Butsugan *

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466 (Japan)

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Abstract

Allylation of a variety of quinones by allylic indium sesquihalides was studied. Reactions of unsubstituted *p*-benzoquinone with allylindium, prenylindium, and geranylindium reagents gave, after oxidation with silver oxide, the corresponding allylated quinones in good yields. These reactions appear to proceed via 1,2-addition of the allylic indium reagents at the γ-carbon followed by [3,3] sigmatropic rearrangement. Substituted quinones reacted with allylindium reagent giving excellent yields of allylquinols, whereas with prenylindium and geranylindium reagents, trisubstituted quinones gave diprenylcyclohexene-1,4-diones and 2,3-disubstituted quinones gave mixtures of prenylhydroquinones and diprenylcyclohexene-1,4-diones. In the prenylation of haloquinones, 1,2-addition, [3,3] sigmatropic rearrangement, and elimination of indium(III) halide occurred in sequence yielding prenylquinones. 2-Hydroxy- and 2-methoxy-1,4-naphthoquinones gave α-addition products with prenylindium and cinnamylindium reagents.

Introduction

Allylation of quinones with allylic organometallic reagents is important not only from a mechanistic standpoint but also for the synthesis of biologically active isoprenoid quinones such as vitamin K, coenzyme Q, and plastoquinone, which play important roles in diverse biological processes, e.g., blood clotting, oxidative phosphorylation, and electron transport in photosynthetic and respiratory systems [1]. A number of synthetic methods for these quinones have hitherto been developed, of which the most straightforward method is the introduction of a polyprenyl chain into a quinonoid nucleus. Existing methods can be classified into the following four categories in regard to the coupling fashion of quinonoid nucleus and polyprenyl chain: (1) Friedel–Crafts type reaction of hydroquinone with polyprenyl alcohol or halide [2], (2) reaction of aryl Grignard reagent or arylcuprate(I) with polyprenyl halide [3], (3) coupling of π-allylnickel(II) complex with halohydroquinone derivative [4], and (4) direct prenylation of quinone by polyprenyl organometallic reagent. The last strategy is particularly fascinating because of its brevity and simplicity. The use of Grignard and organolithium reagents requires protection of quinone in order to suppress the simple reduction of quinone [5]; however, allylzinc [6] and π-allylnickel(II) reagents [7] have been successfully utilized for direct allylation of

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quinones. Allylsilanes [8] and allylstannanes [9] can be used for the direct allylation of unprotected quinones, and stereoselective synthesis of naturally occurring isoprenoid quinones was developed using polyprenylstannanes [9]. However, these reactions require a Lewis-acid catalyst owing to the low nucleophilicity of allylsilanes and allylstannanes.

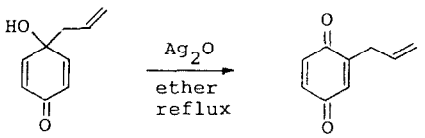
Recently, we reported the preparation of allylindium sesquihalides ($R_3In_2X_3$, R = allyl) [10], and their reactions, i.e., protolysis, oxygenation, and coupling with carbonyl compounds and chlorostannane, were investigated [10,11]. This paper describes a study on the allylation of quinones by allylic indium reagents, aiming at the development of a new synthetic method for the biologically active isoprenoid quinones.

Results and discussion

As it is known that only two of the three allyl groups of allylindium sesquihalides are transferred to carbonyl compounds [10a], allylations of quinones were conducted under a 2:1 molar ratio of quinone:allylindium sesquihalide. Various combinations of quinones and the allylic indium reagents were investigated and it was found that the reaction modes are diverse, depending upon both the type of quinones and the substitution pattern of allylic indium reagents.

Allylation, prenylation, and geranylation of unsubstituted p-*benzoquinone*

The reaction of *p*-benzoquinone with allylindium sesquiiodide at low temperature (ca. −45 °C) gave allyl-*p*-benzoquinone (**1**) in 91% yield after oxidation of the crude product with silver oxide (Table 1). When the reaction was quickly worked up and the crude product was analyzed by ^{1}H NMR, allylquinol (**2**) was detected which was converted to allyl-*p*-benzoquinone (**1**) by refluxing in ether with silver oxide (eq. 1). Prenylindium reagent similarly reacted with *p*-benzoquinone to give prenyl-*p*-benzoquinone (**3**) in 59% yield, after oxidation. The product coupled at the γ-terminus of the prenylindium, (1,1-dimethylprop-2-enyl)-*p*-benzoquinone, was not formed. Geranylation with geranylindium sesquibromide gave geranyl-*p*-benzoquinone (**4**) in 69% yield; however, the product was a mixture of geometrical isomers with an *E*:*Z* ratio of 53:47. By using nerylindium reagent, the same compound **4** with an *E*:*Z* ratio of 44:56 was obtained. An attempt to improve the stereoselectivity by changing the reaction temperature failed.

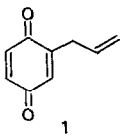
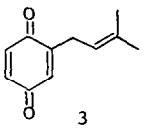
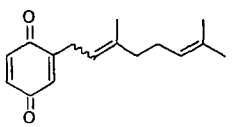


2 1 (1)

In the Lewis acid-catalyzed polyprenylation of *p*-benzoquinone with polyprenylstannanes, an α-addition–[1,3]sigmatropic rearrangement mechanism is proposed [9c,9e]. In such a mechanism, the stereochemistry of the allylic double bond is known to be maintained. The observed complete loss of the stereochemistry in our indium-induced geranylation and nerylation suggests that the α-addition–[1,3] migration mechanism is very unlikely. Scheme 1 illustrates the plausible reaction

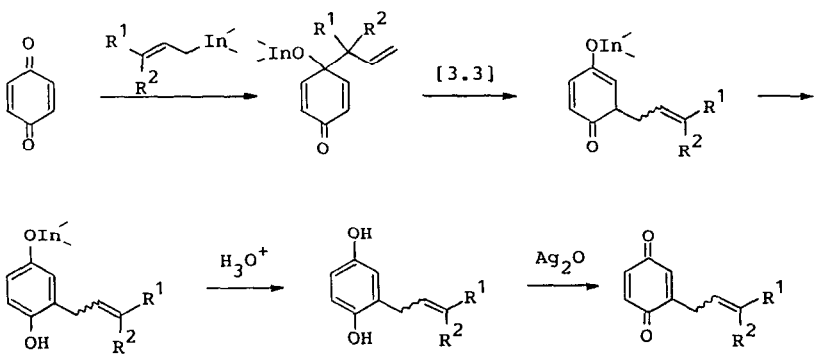
Table 1

Allylation, prenylation, and geranylation of *p*-benzoquinone

Allylindium	Product[a]	Yield, %
Allyl	 1	91
Prenyl	 3	59
Geranyl	 4	69[b]
Neryl	4	58[c]

[a] After oxidation with Ag_2O. [b] $E:Z = 53:47$. [c] $E:Z = 44:56$.

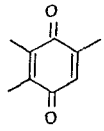
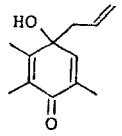
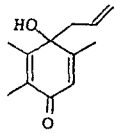
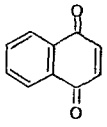
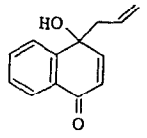
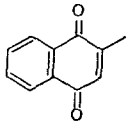
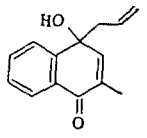
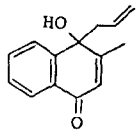
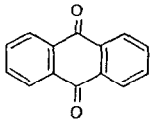
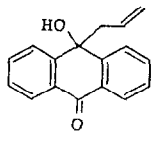
pathway of the allylations of *p*-benzoquinone with the allylic indium reagents. 1,2-Addition of the allylindium reagents to a quinone carbonyl gives the indium salts of allylquinol. In analogy with simple carbonyl compounds [10,11], this addition is considered to proceed at the γ-terminus of the allylic indium reagents. [3,3] Sigmatropic rearrangement of the resulting allylquinol indium salts gives allylhydroquinones after aqueous workup. This rearrangement is facile in particular when R^1 and R^2 are large substituents in order to relieve steric interactions.



Scheme 1

Table 2

Allylation of substituted quinones

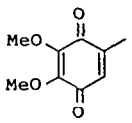
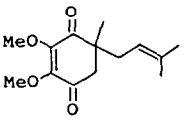
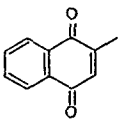
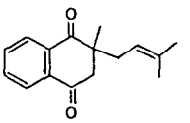
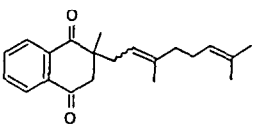
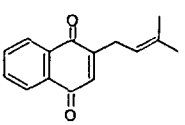
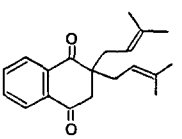
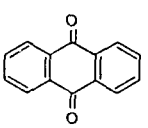
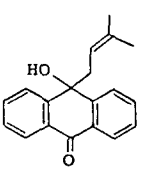
Quinone	Product	Yield, %
	 5	76
	 6	23
	 7	100
	 8	61
	 9	39
	 10	100

Allylation of substituted p-*quinones*

Substituted quinones such as trimethyl-*p*-benzoquinone, 1,4-naphthoquinone, and anthraquinone were reacted with allylindium sesquiiodide to give allylquinols **5–10** in excellent yields (Table 2). The asymmetrically substituted quinones gave two possible quinols; the less-hindered carbonyl group was preferentially attacked

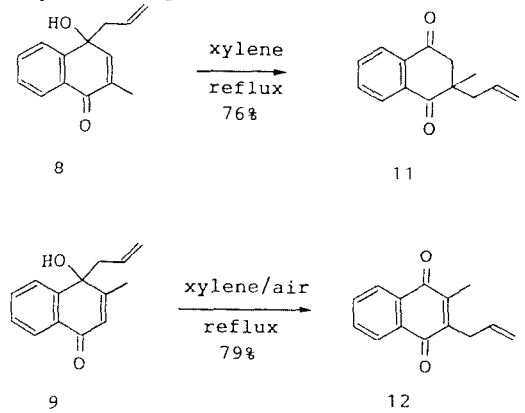
Table 3

Prenylation and geranylation of tri- and tetrasubstituted quinones

Quinone	Allylindium	Product	Yield, %
	Prenyl	 16	100
	Prenyl	 17	100
"	Geranyl	 18	85[a]
"	Neryl	18	95[b]
	Prenyl	 19	100
	Prenyl	 20	31

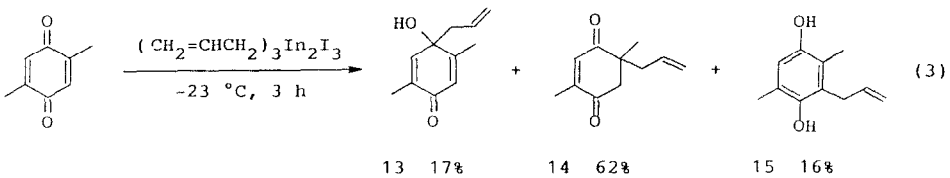
[a] $E:Z = 56:44$. [b] $E:Z = 59:41$.

by the indium reagent. The resulting allylquinols **8** and **9** underwent [3,3] sigmatropic rearrangement at an elevated temperature to give **11** and **12**, respectively (eq. 2).



(2)

2). Allylation of 2,5-dimethyl-*p*-benzoquinone gave allylquinol **13** in 17% yield together with cyclohexene-1,4-dione **14** and hydroquinone **15** in 62 and 16% yields, respectively (eq. 3).



(3)

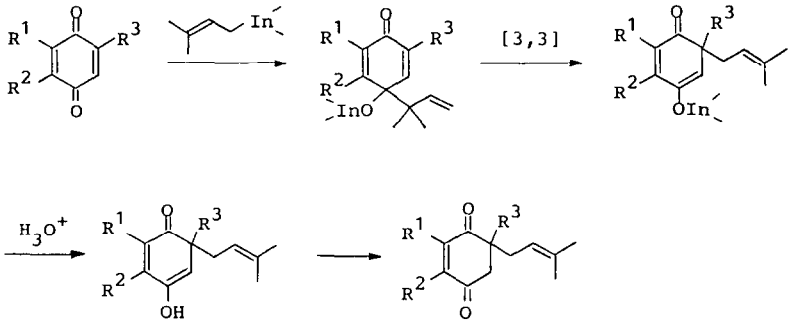
13 17% 14 62% 15 16%

Prenylation and geranylation of substituted p*-quinones*

As shown in Table 3, prenylation and geranylation of trisubstituted *p*-benzoquinones and 2-substituted 1,4-naphthoquinones gave the corresponding cyclohexene-1,4-diones **16**–**19** in high yields. No other regioisomers were found in the reaction mixtures. These results indicate again that the coupling is highly regiospecific in regard to both the quinone carbonyl and the allylic terminus. The following mechanism for the formation of **16**–**19** seems to be most probable: addition at the γ-carbon of the prenyl and geranylindium reagents to the less-hindered quinone carbonyl followed by [3,3] sigmatropic rearrangement furnishes total addition at the α-carbon of the allylic system to the adjacent carbon of the hindered carbonyl (Scheme 2).

Prenylation of anthraquinone, a representative of tetrasubstituted quinones, is sluggish; after 20 h at room temperature α-prenylated anthraquinol **20** was obtained in 31% yield (Table 3). γ-Prenylated products were not found in this reaction. This first example of α-addition of allylic indium reagents to carbonyl compounds is attributable to the difficulty of the γ-addition owing to steric crowding.

Results for prenylation and nerylation of 2,3-disubstituted quinones are summarized in Table 4. In all cases, considerable amounts of diprenylated products **19**, **23**, **25**, and **27** were obtained together with monoprenylhydroquinones, which were isolated as the corresponding prenylquinones **21**, **22**, **24**, and **26** after oxidation with silver oxide. Quinone **21** is the naturally occurring deoxylapachol [12] and compounds **24** and **26** are plastoquinones. Varying the ratio charged quinone : pre-



Scheme 2

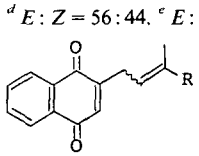
nylindium greatly affected the monoprenyl : diprenyl selectivity of the products; both decreasing and increasing the ratio quinone : prenylindium improved the selectivity of the monoprenylhydroquinone. A plausible mechanism is illustrated in

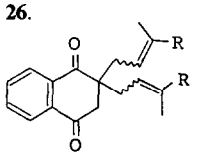
Table 4

Prenylation and nerylation of 2,3-disubstituted quinones

Quinone	Allyl-indium	Molar ratio quinone : allylindium	Product [a]			Total yield [b] (%)
			mono-allyl	di-allyl	ratio	
1,4-Naphthoquinone	Prenyl	1:1	**21**	**19**	61:39	86 [c]
		2:1			22:78	100
		4:1			77:23	79
		6:1			97:3	100
	Neryl	2:1	**22**	**23**	29:71	92
		3:1			71:29	97
		6:1			100:0	84 [d]
2,3-Dimethyl-*p*-benzoquinone	Prenyl	2:1	**24**	**25**	54:46	45
	Neryl	2:1	**26**	**27**	64:36	64 [e]

[a] After oxidation with Ag_2O. [b] Based on allylindium, unless otherwise noted. [c] Based on quinone. [d] $E:Z = 56:44$. [e] $E:Z = 74:26$ for **26**.



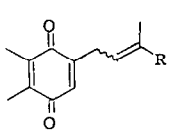


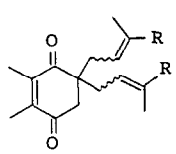
21 R = Me

22 = $(CH_2)_2CH{=}CMe_2$

19 R = Me

23 = $(CH_2)_2CH{=}CMe_2$



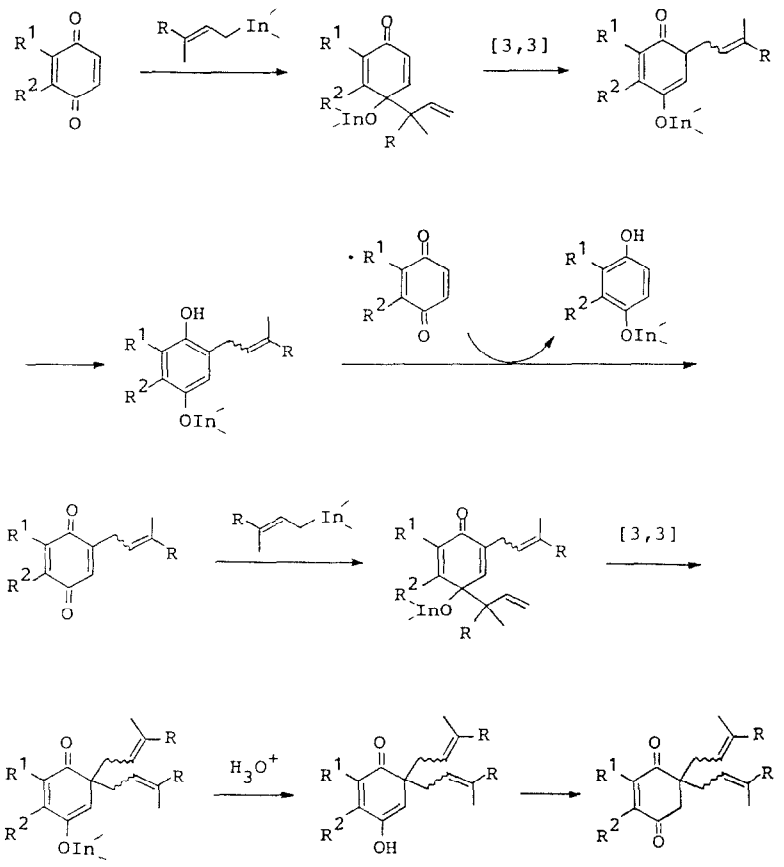


24 R = Me

26 = $(CH_2)_2CH{=}CMe_2$

25 R = Me

27 = $(CH_2)_2CH{=}CMe_2$



Scheme 3

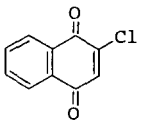
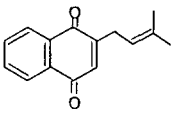
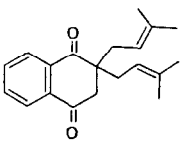
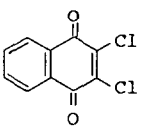
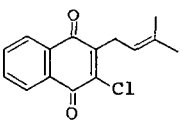
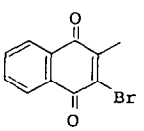
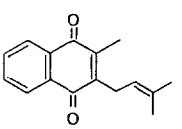
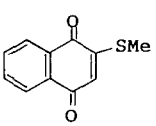
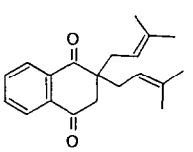
Scheme 3. γ-Attack of prenylindium reagent followed by [3,3] sigmatropic rearrangement affords prenylhydroquinone indium salt which is oxidized *in situ* by the starting quinone giving monoprenylquinone. The second addition of prenylindium to the less-hindered carbonyl of the resulting monoprenylquinone and subsequent [3,3] sigmatropic rearrangement furnish diprenylcyclohexene-1,4-dione. The use of an excess amount of quinone suppresses the second prenylation and an insufficient amount of quinone prevents the oxidation of monoprenylhydroquinone indium salt to the corresponding prenylquinone; consequently the monoprenyl vs. diprenyl selectivity is increased in both cases.

Prenylation of haloquinones

Prenylation of 2-chloro-1,4-naphthoquinone with prenylindium sesquibromide gave a mixture of two chlorine-free products, 2-prenyl-1,4-naphthoquinone (**21**) and 2,3-benzo-5,5-diprenylcyclohexane-1,4-dione (**19**) in 53 and 37% yields, respectively (Table 5). This selectivity (**21** : **19** = 53 : 37) couldbe easily improved to 72 : 6 merely by using a 1.5-fold excess of the quinone. It was reported that the zinc-mediated reaction of the same quinone with prenyl bromide afforded two chlorine-containing products, 2-chloro-3-prenyl-1,4-naphthoquinone and 2,3-benzo-5-chloro-6,6-dipre-

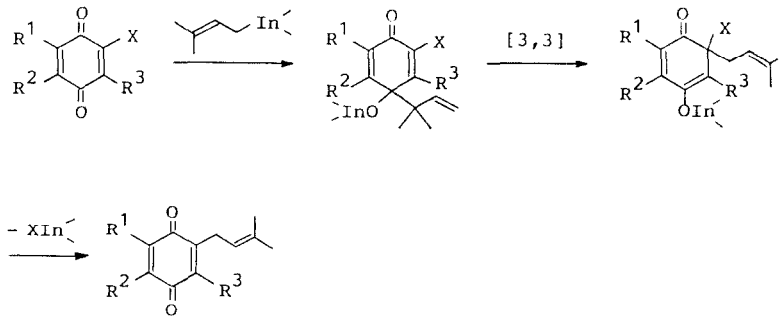
Table 5

Prenylation of haloquinones

Quinone	Product	Yield, %
	 21	53 (72)[a]
	 19	37 (6)[a]
	 28	100
	 29	67
	 19	31

[a] For a reaction with quinone (3 mmol) and prenylindium (1 mmol).

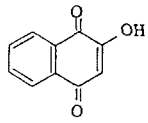
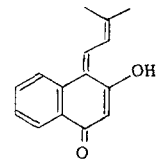
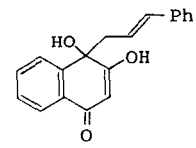
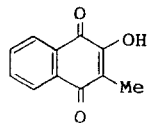
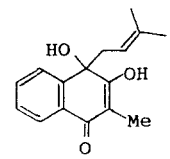
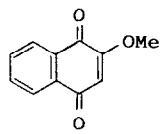
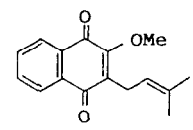
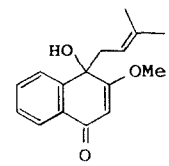
nylcyclohexane-1,4-dione in low yields [6c]. Furthermore, the crotylation of 2,3-dichloro-*p*-benzoquinone by tributylcrotylstannane also gave chlorine-containing products [9c]. This marked contrast of the reaction of the allylic indium reagent compared with those of the zinc and tin reagents is a good example of the synthetic usefulness of organoindium reagents. 2,3-Dichloro- and 2-bromo-3-methyl-1,4-naphthoquinones gave similar monoprenylated 1,4-naphthoquinones, **28** and **29**, selectively in good yields. Product **28** is a useful precursor to lapachol [6c], and **29** is vitamin K_2 itself. These prenylated quinones are considered to be formed as shown in Scheme 4: γ-prenylation and [3,3] sigmatropic rearrangement give an indium



Scheme 4

Table 6

Prenylation and cinnamylation of hydroxyquinones

Quinone	Allylindium	Product	Yield, %
	prenyl	 30	59
"	cinnamyl	 31	72
	prenyl	 32	97
	prenyl	 33	43
		 34	40

enolate intermediate which eliminates indium(III) halide giving prenylated quinone. 2-Methylthio-1,4-naphthoquinone was also prenylated by prenylindium, but the product was only **19** in a low yield owing to the poor leaving nature of methylthio group.

Prenylation and cinnamylation of hydroxyquinones

Upon prenylation, 2-hydroxy-1,4-naphthoquinone gave 3-hydroxy-4-(3-methyl-2-butenylidene)naphthalen-1-one (**30**) as the sole isolable product in 59% yield (Table 6). Compound **30** is obviously a dehydration product of the corresponding prenylquinol, an α-prenylation product. Indeed, cinnamylation of the same quinone gave α-cinnamylated quinol **31** in good yield. ^{1}H and ^{13}C NMR analysis revealed that compound **31** exists predominantly as the enol form in polar solvents such as dimethylsulfoxide and methanol, and as the diketone tautomer in less-polar solvents such as chloroform. 2-Hydroxy-3-methyl-1,4-naphthoquinone also gave α-prenylation product **32**. 2-Methoxy-1,4-naphthoquinone afforded two prenylation products, prenylquinone **33** and prenylquinol **34**, in 43 and 40% yields, respectively. Compound **33** may be rationalized as a γ-addition–[3,3] migration product and **34** is an α-addition product corresponding to **30**, **31**, and **32**. Prenylation of 2-methoxy-1,4-naphthoquinone by tributylprenylstannane was reported to afford the same products **33** and **34**, but the yields were poor (7–10%) [9c]. Compounds **30**, **31**, **32**, and **34** are further examples of the α-addition of allylic indium reagents to carbonyl compounds. In these reactions, hydroxyl and methoxy groups do not function as a leaving group but their electron-donating nature deactivates the C-4 carbonyl, and consequently orientates the allylic indium reagents to the sterically crowded C-1 carbonyl. In these cases, the prenylindium reagent reacts at the α-carbon, because γ-addition suffers from more serious steric interactions.

In summary, reactions of allylic indium reagents with a variety of quinones have been studied. In general, allylic indium reagents regioselectively attack a less-hindered carbonyl group of quinones at the γ-carbon giving allylic quinols, which undergo facile [3,3] sigmatropic rearrangement giving indium enolates. Depending on the substitution pattern, the enolates after hydrolysis afford allylated hydroquinones or cyclohexene-1,4-diones. When they possess a good leaving group such as halogen, spontaneous elimination of indium(III) halide occurs to afford allylated quinones. Only when severe steric interactions are present, allylic indium reagents react at the α-carbon.

Unfortunately, the present indium-mediated allylation of quinones lacks stereoselectivity in respect of the introduced allylic double bond. This is a serious disadvantage for the synthesis of biologically active isoprenoid quinones, in which the polyprenyl side chain possesses an *E*-geometry. Nevertheless, our allylation of quinones by allylic indium reagents is important not only because of its unique reaction modes, high regioselectivity, and the good yields but also as a demonstration of the usefulness of organoindium reagents in organic synthesis.

Experimental

General

Mass spectra (MS) were recorded by electron impact ionization. Indium powder, stabilized by 0.5% of MgO, was purchased from Nacalai Tesque Co. Ltd. DMF was

distilled from CaH_2 under vacuum and stored over CaH_2. All reactions were conducted under argon unless otherwise stated.

Allylation of p-*benzoquinone*

To a stirred solution of allylindium sesquiiodide, prepared from indium powder (230 mg, 2 mmol) and allyl iodide (504 mg, 3 mmol) in DMF (1 ml) according to the published method [10b], was added *p*-benzoquinone (216 mg, 2 mmol) in DMF (2 ml) at −45 °C. The mixture was stirred in the dark at −41 – −48 °C for 3 h. Water was added and the product was extracted with ether. The extracts were washed with water, brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure. ^1H NMR analysis of the crude product revealed that it was almost pure allylquinol (**2**) [^1H NMR (60 MHz, CCl_4) δ 2.53 (d, $J = 7$ Hz, 2H, CH_2), 3.87 (bs, 1H, OH), 5.08 (m, 1H, allyl), 5.29 (m, 1H, allyl), 5.70 (1H, m, allyl), 6.25 (d, $J = 11$ Hz, 2H, ring H), 7.08 (d, $J = 11$ Hz, 2H, ring H)], but during purification it partly rearranged to allylhydroquinone: m.p. 90–91 °C (lit. [7b] 92–93 °C). The crude product was refluxed for 1 h with Ag_2O (0.7 g) and anhydrous Na_2SO_4 (2 g) in ether (6 ml). The mixture was filtered and the filtrate was subjected to column chromatography on silica gel (CH_2Cl_2–ether gradient) to give *allyl*-p-*benzoquinone* (***1***) [9a] (270 mg, 91%). Yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 3.22 (dd, $J = 8$, 1 Hz, 2H, CH_2), 5.15–5.36 (m, 2H, olefinic), 5.75–6.02 (m, 1H, olefinic), 6.62 (q, $J = 1$ Hz, 1H, ring H), 6.79 (dd, $J = 10$, 1 Hz, 1H, ring H), 6.82 (d, $J = 10$ Hz, 1H, ring H); IR (neat) 1658 cm^{-1} (C=O).

Reactions of *p*-benzoquinone with prenylindium, geranylindium, and nerylindium reagents were similarly carried out and the products similarly worked up. The results are shown in Table 1.

Prenyl-p-*benzoquinone (**3**).* Yellow oil (lit. [9c] m.p. 29–30 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 1.66 (s, 3H, Me), 1.79 (s, 3H, Me), 3.15 (bd, $J = 8$ Hz, 2H, CH_2), 5.19 (bt, $J = 8$ Hz, 1H, olefinic), 6.56 (q, $J = 1$ Hz, 1H, ring H), 6.76 (dd, $J = 10$, 1 Hz, 1H, ring H), 6.80 (d, $J = 10$ Hz, 1H, ring H); IR (neat) 1660 cm^{-1} (C=O).

3,7-Dimethylocta-2,6-dienyl-p-*benzoquinone (**4**) [9d] (E : Z = 53 : 47).* Yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60, 1.62, 1.66, 1.70, 1.77 (each s, total 9H, Me), 1.90–2.26 (m, 4H, CH_2), 3.14 (bd, $J = 7$ Hz, 2H, CH_2), 5.10 (bs, 1H, olefinic), 5.18 (t, $J = 7$ Hz, 1H, olefinic), 6.56 (q, $J = 1$ Hz, 1H, ring H), 6.74 (dd, $J = 10$, 1 Hz, 1H, ring H), 6.78 (d, $J = 10$ Hz, 1H, ring H); IR (neat) 1660 cm^{-1} (C=O). The $E : Z$ ratio was estimated from the ^1H NMR results, based on the integration of the δ 1.70 (*E*-isomer) and 1.77 signals (*Z*-isomer) [9d]. The reaction with nerylindium reagent gave the same product ($E : Z = 44 : 56$).

Allylation of substituted quinones

The following allylation of trimethyl-*p*-benzoquinone represents the general procedure. However, the allylation of anthraquinone was conducted at 20 °C for 3 h.

Trimethyl-*p*-benzoquinone (301 mg, 2 mmol) was added to allylindium sesquiiodide prepared from indium (230 mg, 2 mmol) and allyl iodide (505 mg, 3 mmol) in DMF (3 ml), and the mixture was stirred at −23 °C for 3 h. Water was added and the products were extracted with ether. The extracts were washed with water, brine and dried (Na_2SO_4). Evaporation of the solvent and column chromatography on silica gel (CH_2Cl_2 : ether = 9 : 1) afforded **5** (288 mg, 76%) and **6** (88 mg, 23%).

1-Allyl-1-hydroxy-2,3,5-trimethylcyclohexa-2,4-dien-4-one (5) [9c]. Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.78 (s, 3H, Me), 1.81 (s, 3H, Me), 1.96 (s, 3H, Me), 2.48 (d, $J = 8$ Hz, 2H, CH_2), 3.19 (bs, 1H, OH), 4.96–5.06 (m, 2H, olefinic), 5.27–5.53 (m, 1H, olefinic), 6.58 (q, $J = 2$ Hz, 1H, ring H); IR (neat) 3410 (OH), 1675 cm^{-1} (C=O).

1-Allyl-1-hydroxy-2,3,6-trimethylcyclohexa-2,4-dien-4-one (6) [9c]. Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 3H, Me), 1.99 (s, 3H, Me), 2.01 (s, 3H, Me), 2.52 (d, $J = 8$ Hz, 2H, CH_2), 3.54 (bs, 1H, OH), 4.84–4.01 (m, 2H, olefinic), 5.01–5.24 (m, 1H, olefinic), 5.91 (bs, 1H, ring H); IR (neat) 3380 (OH), 1668 cm^{-1} (C=O).

2,3-Benzo-1-allyl-1-hydroxycyclohexa-2,5-dien-4-one (7). Colourless crystals; m.p. 79.5–80.0 °C (lit. [13] m.p. 81–82 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.66 (m, 2H, CH_2), 3.44 (bs, 1H, OH), 4.86–5.04 (m, 2H, olefinic), 5.29–5.54 (m, 1H, olefinic), 6.24 (d, $J = 11$ Hz, 1H, ring H), 6.94 (d, $J = 11$ Hz, ring H), 7.41 (t, $J = 8$ Hz, 1H, Ar), 7.63 (t, $J = 8$ Hz, 1H, Ar), 7.74 (d, $J = 8$ Hz, 1H, Ar), 7.96 (d, $J = 8$ Hz, Ar); IR (KBr) 3370 (OH), 1660 cm^{-1} (C=O).

2,3-Benzo-1-allyl-1-hydroxy-4-methylcyclohexa-2,4-dien-4-one (8). Colourless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.85 (d, $J = 2$ Hz, 3H, Me), 2.63 (d, $J = 7$ Hz, 2H, CH_2), 3.73 (s, 1H, OH), 4.80–5.02 (m, 2H, olefinic), 5.23–5.50 (m, 1H, olefinic), 6.70 (q, $J = 2$ Hz, 1H, ring H), 7.34 (t, $J = 8$ Hz, 1H, Ar), 7.56 (t, $J = 8$ Hz, 1H, Ar), 7.67 (d, $J = 8$ Hz, 1H, Ar), 7.90 (d, $J = 8$ Hz, 1H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.4 (q), 47.5 (t), 70.0 (s), 119.0 (t), 125.8 (d), 125.9 (d), 127.4 (d), 129.6 (s), 131.1 (d), 132.4 (d), 133.9 (s), 146.2 (s), 147.6 (d), 185.1 (s); IR (neat) 3430 (OH), 1662, 1642 cm^{-1} (C=O); MS (70 eV) m/z 214 (M^+); Anal. Found: C, 78.38; H, 6.36. $C_{14}H_{14}O_2$ clac.: C, 78.48; H, 6.59%.

2,3-Benzo-1-allyl-1-hydroxy-6-methylcyclohexa-2,4-dien-4-one (9). Colourless crystals; m.p. 127.5–128.0 °C (hexane–AcOEt); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.08 (d, $J = 2$ Hz, 3H, Me), 2.68 (m, 2H, CH_2), 3.47 (s, 1H, OH), 4.66–4.86 (m, 2H, olefinic), 4.90–5.17 (m, 1H, olefinic), 5.96 (q, $J = 2$ Hz, 1H, ring H), 7.36 (t, $J = 8$ Hz, 1H, Ar), 7.58 (t, $J = 8$ Hz, 1H, Ar), 7.74 (d, $J = 8$ Hz, 1H, Ar), 7.88 (d, $J = 8$ Hz, 1H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.3 (q), 46.6 (t), 73.6 (s), 119.3 (t), 125.6 (d), 125.9 (d), 127.4 (d), 127.8 (d), 130.6 (d), 132.7 (d), 146.8 (s), 161.4 (s), 184.2 (s); IR (neat) 3370 (OH), 1650 cm^{-1} (C=O); MS (70 eV) m/z 214 (M^+); Anal. Found: C, 78.56; H, 6.46. $C_{14}H_{14}O_2$ calc.: C, 78.48; H, 6.59%.

9-Allyl-9-hydroxy-10-oxoanthracene (10). Colourless crystals; m.p. 94 °C (lit. [14] m.p. 100.5–101 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.51 ($J = 8$ Hz, 2H, CH_2), 4.40 (dd, $J = 17$, 2 Hz, 1H, olefinic), 4.62 (dd, $J = 10$, 2 Hz, 1H, olefinic), 4.78–5.08 (m, 1H, olefinic), 4.82 (s, 1H, OH), 7.25 (t, $J = 8$ Hz, 2H, Ar), 7.48 (t, $J = 8$ Hz, 2H, Ar), 7.74 (d, $J = 8$ Hz, 2H, Ar), 7.83 (d, $J = 8$ Hz, 2H, Ar); IR (KBr) 3462 (OH), 1650 cm^{-1} (C=O).

1-Allyl-1-hydroxy-2,5-dimethylcyclohexa-2,4-dien-4-one (13). Pale yellow crystals; m.p. 60 °C (hexane–AcOEt); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.87 (d, $J = 2$ Hz, 3H, Me), 2.05 (d, $J = 2$ Hz, 3H, Me), 2.54 (d, $J = 8$ Hz, 2H, CH_2), 2.74 (bs, 1H, OH), 5.05–5.14 (m, 2H, olefinic), 5.38–5.77 (m, 1H, olefinic), 6.03 (q, $J = 2$ Hz, 1H, ring H), 6.62 (q, $J = 2$ Hz, 1H, ring H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.1 (q), 17.6 (q), 43.1 (t), 71.7 (s), 119.2 (t), 127.0 (d), 130.9 (d), 134.8 (s), 146.5 (d), 160.0 (s), 186.4 (s); IR (KBr) 3460 (OH), 1672 cm^{-1} (C=O); MS (70 eV) m/z 178 (M^+); Anal. Found: C, 73.87; H, 8.03. $C_{11}H_{14}O_2$ calc.: C, 74.13; H, 7.92%.

*5-Allyl-2,5-dimethylcyclohex-2-ene-1,4-dione (**14**).* Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (s, 3H, Me), 2.01 (d, $J = 2$ Hz, 3H, Me), 2.19 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.48 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.64 (d, $J = 16$ Hz, 1H, ring CH_2), 2.88 (d, $J = 16$ Hz, 1H, ring CH_2), 5.01–5.18 (m, 2H, olefinic), 5.58–5.83 (m, 1H, olefinic), 6.53 (q, $J = 2$ Hz, 1H, ring H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.8 (q), 24.3 (q), 43.2 (t), 49.0 (t), 76.4 (s), 119.4 (t), 132.8 (d), 136.4 (d), 149.9 (s), 198.6 (s), 202.3 (s); IR (KBr) 1685 cm^{-1} (C=O); MS (70 eV) *m/z* 178 (M^+); Anal. Found: C, 74.04; H, 8.00. $C_{11}H_{14}O_2$ calc.: C, 74.13; H, 7.92%.

*2-Allyl-3,6-dimethylhydroquinone (**15**).* Colourless crystals; m.p. 136–137 °C (lit. [9c] m.p. 141–142 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.17 (s, 3H, Me), 2.18 (s, 3H, Me), 3.44 (d, $J = 6$ Hz, 2H, CH_2), 4.49 (bs, 2H, OH), 5.00–5.20 (m, 2H, olefinic), 5.89–6.09 (m, 1H, olefinic), 6.52 (2, 1H, Ar); IR (KBr) 3260 cm^{-1} (OH).

*[3,3] Sigmatropic rearrangement of allylquinols **8** and **9***

Allylquinol **8** (107 mg, 0.5 mmol) was refluxed in xylene (5 ml) for 15 h. The product was purified by column chromatography on silica gel (CH_2Cl_2) to give **11** (82 mg, 76%). Rearrangement of **9** was similarly performed (under air) and **12** was obtained in 79% yield.

*2,3-Benzo-5-allyl-5-methylcyclohexane-1,4-dione (**11**).* Yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (s, 3H, Me), 2.28 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.55 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.86 (d, $J = 16$ Hz, 1H, ring CH_2), 3.05 (d, $J = 16$ Hz, 1H, ring CH_2), 4.98–5.16 (m, 2H, olefinic), 5.62–5.85 (m, 1H, olefinic), 7.77 (m, 2H, Ar), 8.07 (m, 2H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.7 (q), 42.9 (t), 48.7 (s), 49.4 (t), 119.4 (t), 126.0 (d), 127.5 (d), 132.7 (d), 133.8 (s), 134.0 (d), 134.4 (d), 134.9 (s), 196.3 (s), 200.3 (s); IR (neat) 1695 cm^{-1} (C=O); MS (70 eV) *m/z* 214 (M^+); Anal. Found: C, 78.47; H, 6.45. $C_{14}H_{14}O_2$ calc.: C, 78.48; H, 6.60%.

*2-Allyl-3-methyl-1,4-naphthoquinone (**12**).* Yellow crystals; m.p. 80–81 °C (lit. [15] m.p. 76 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.20 (s, 3H, Me), 3.43 (d, $J = 4$ Hz, 2H, CH_2), 5.08–5.10 (m, 2H, olefinic), 5.78–5.97 (m, 1H, olefinic), 7.73 (m, 2H, Ar), 8.10 (m, 2H, Ar); IR (KBr) 1662 cm^{-1} (C=O).

Prenylation and geranylation of tri- and tetrasubstituted quinones

These reactions were carried out similarly to the allylations of substituted quinones described above. Only the prenylation of anthraquinone was conducted at 20 °C for 20 h.

*2,3-Dimethoxy-5-methyl-5-(3-methyl-2-butenyl)cyclohex-2-ene-1,4-dione (**16**) [7b].* Yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (s, 3H, ring Me), 1.58 (s, 3H, Me), 1.69 (s, 3H, Me), 2.21 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.38 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.55 (d, $J = 16$ Hz, 1H, ring CH_2), 2.76 (d, $J = 16$ Hz, 1H, ring CH_2), 3.97 (s, 3H, OMe), 4.00 (s, 3H, OMe), 5.03 (t, $J = 8$ Hz, 1H, olefinic); IR (neat) 1680 cm^{-1} (C=O).

*2,3-Benzo-5-methyl-5-(3-methyl-2-butenyl)cyclohexane-1,4-dione (**17**) [9c].* Pale yellow oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (s, 3H, ring Me), 1.51 (s, 3H, Me), 1.64 (s, 3H, Me), 2.27 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.47 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.86 (d, $J = 16$ Hz, 1H, ring CH_2), 3.04 (d, $J = 16$ Hz, 1H, ring CH_2), 5.06 (t, $J = 8$ Hz, 1H, olefinic), 7.76 (m, 2H, Ar), 8.08 (m, 2H, Ar); IR (neat) 1694 cm^{-1} (C=O).

*2,3-Benzo-5-methyl-5-(3,7-dimethylocta-2,6-dienyl)-cyclohexane-1,4-dione (**18**) [9d] (E : Z = 56 : 44).* Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (s, 3H, ring

Me), 1.50 (s, 3H, Me), 1.56 (s, 3H, Me), 1.62 and 1.66 (each s, total 3H, Me), 1.97 (m, 4H, CH_2), 2.27 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.47 (dd, $J = 14$, 8 Hz, 1H, CH_2), 2.85 (d, $J = 16$ Hz, 1H, ring CH_2), 3.03 (d, $J = 16$ Hz, 1H, ring CH_2), 5.05 (m, 2H, olefinic), 7.78 (m, 2H, Ar), 8.08 (m, 2H, Ar); IR (neat) 1694 cm^{-1} (C=O). The $E:Z$ ratio was estimated from the ^1H NMR results, based on the integration of the δ 1.62 (E-isomer) and 1.66 signals (Z-isomer) [9d].

*2,3-Benzo-5,5-di(3-methyl-2-butenyl)cyclohexane-1,4-dione (**19**) [6c].* Pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.52 (s, 6H, Me), 1.62 (s, 6H, Me), 2.29 (dd, $J = 14$, 8 Hz, 2H, CH_2), 2.51 (dd, $J = 14$, 8 Hz, 2H, CH_2), 2.94 (s, 2H, ring CH_2), 5.04 (t, $J = 8$ Hz, 2H, olefinic), 7.76 (m, 2H, Ar), 8.10 (m, 2H, Ar); IR (neat) 1696 cm^{-1} (C=O).

*10-Hydroxy-10-(3-methyl-2-butenyl)-9(10H)-anthracene (**20**) [16].* Colourless crystals; m.p. 138–139 °C (lit. [16] m.p. 142–143 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 0.85 (s, 3H, Me), 1.40 (s, 3H, Me), 2.30 (bs, 1H, OH), 2.60 (d, $J = 8$ Hz, 2H, CH_2), 4.20 (t, $J = 8$ Hz, 1H, olefinic), 7.20–7.75 (m, 4H, Ar), 7.93 (m, 2H, Ar), 8.20 (m, 2H, Ar); IR (KBr) 3475 (OH), 1654 cm^{-1} (C=O).

Prenylation and nerylation of 2,3-disubstituted quinones

These reactions were carried out under varying quinone : allylic indium ratios. The results are summarized in Table 4. The following reaction of 1,4-naphthoquinone and prenylindium in a 1 : 1 ratio represents the general procedure.

To a solution of prenylindium sesquibromide (1 mmol) prepared from indium (233 mg, 2 mmol) and prenyl bromide (448 mg, 3 mmol) in DMF (1 ml) was added 1,4-naphthoquinone (318 mg, 2 mmol) in DMF (2 ml) at −23 °C, and the mixture was stirred at −23 °C for 3 h. Usual aqueous workup and oxidation with Ag_2O gave the crude product which was subjected to column chromatography (silica gel/benzene) to give a mixture of **21** and **19** (155 mg, 86%; **21** : **19** = 61 : 39 by ^1H NMR). Pure samples of **21** and **19** were obtained by repeated column chromatography.

*2-(3-Methyl-2-butenyl)-1,4-naphthoquinone (**21**).* Yellow crystals; m.p. 60–62 °C (lit. [6c] m.p. 60–62 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 1.68 (s, 3H, Me), 1.80 (s, 3H, Me), 3.29 (d, $J = 8$ Hz, 2H, CH_2), 5.25 (t, $J = 8$ Hz, 1H, olefinic), 6.80 (t, $J = 1$ Hz, ring H), 7.76 (m, 2H, Ar), 8.10 (m, 2H, Ar); IR (KBr) 1660 cm^{-1} (C=O).

*2-(3,7-Dimethylocta-2,6-dienyl)-1,4-naphthoquinone (**22**) [17] (E : Z = 56 : 44).* A yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60, 1.62, 1.66 (each s, total 6H, Me), 1.71, 1.80 (each s, total 3H, Me), 2.11 (m, 4H, CH_2), 3.30 (d, $J = 8$ Hz, 2H, CH_2), 5.12 (m, 1H, olefinic), 5.25 (t, $J = 8$ Hz, 1H, olefinic), 6.80 (m, 1H, ring H), 7.75 (m, 2H, Ar), 8.10 (m, 2H, Ar); IR (neat) 1664 cm^{-1} (C=O). The $E:Z$ ratio was estimated from the ^1H NMR results, based on the integration of the δ 1.71 (E-isomer) and 1.80 signals (Z-isomer).

*2,3-Benzo-5,5-di(3,7-dimethylocta-2,6-dienyl)cyclohexane-1,4-dione (**23**) (E : Z mixture).* Pale yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.52, 1.55, 1.58, 1.60, 1.64, 1.67 (each s, total 9H, Me), 1.82–2.16 (m, 4H, CH_2), 2.29 (dd, $J = 16$, 8 Hz, 2H, CH_2), 2.52 (dd, $J = 16$, 8 Hz, 2H, CH_2), 2.94 (s, 2H, ring CH_2), 5.04 (m, 4H, olefinic), 7.75 (m, 2H, Ar), 8.08 (m, 2H, Ar); IR (neat) 1692 cm^{-1} (C=O); Anal. Found: C, 83.26; H, 9.42. $C_{30}H_{40}O_2$ calc.: C, 83.28; H, 9.32%. The $E:Z$ ratio was not determined.

*2,3-Dimethyl-5-(3-methyl-2-butenyl)benzoquinone (**24**) [9a].* Yellow oil; ^1H NMR

(200 MHz, $CDCl_3$) δ 1.64 (s, 3H, Me), 1.77 (s, 3H, Me), 2.02 (s, 3H, ring Me), 2.04 (s, 3H, ring Me), 3.12 (d, $J = 8$ Hz, 2H, CH_2), 5.17 (t, $J = 8$ Hz, 1H, olefinic), 6.50 (t, $J = 1$ Hz, 1H, ring H); IR (neat) 1650 cm^{-1} (C=O).

2,3-Dimethyl-5-di(3-methyl-2-butenyl)cyclohex-2-ene-1,4-dione ***(25)***. Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55 (s, 6H, Me), 1.66 (s, 6H, Me), 1.98 (s, 6H, ring Me), 2.19 (dd, $J = 14$, 8 Hz, 2H, CH_2), 2.38 (dd, $J = 14$, 8 Hz, 2H, CH_2), 2.71 (s, 2H, ring CH_2), 4.99 (t, $J = 8$ Hz, 2H, olefinic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.7 (q), 13.2 (q), 17.9 (q), 25.9 (q), 36.6 (t), 46.3 (t), 53.4 (s), 119.1 (d), 135.7 (s), 144.9 (s), 145.3 (s). 198.3 (s), 201.9 (s); IR (neat) 1676 cm^{-1} (C=O); MS (70 eV) m/z 274 (M^+); Anal. Found: C, 78.80; H, 9.62. $C_{18}H_{26}O_2$ calc.: C, 78.79; H, 9.55%.

2,3-Dimethyl-5-(3,7-dimethylocta-2,6-dienyl)-1,4-naphthoquinone ***(26)*** *[17] (E : Z = 74 : 36).* Yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62, 1.67 (each s, total 6H, Me), 1.71, 1.77 (each s, total 3H, Me), 2.02 (s, 3H, Me), 2.04 (s, 3H, Me), 2.08 (m, 4H, CH_2), 3.14 (d, $J = 8$ Hz, 2H, CH_2), 5.10 (bs, 1H, olefinic), 5.17 (t, $J = 8$ Hz, 1H, olefinic), 6.49 (t, $J = 1$ Hz, ring H); IR (neat) 1647 cm^{-1} (C=O). The $E : Z$ ratio was estimated by the ^{1}H NMR based on the integration of the δ 1.71 (*E*-isomer) and 1.77 signals (*Z*-isomer).

2,3-Dimethyl-5,5-di(3,7-dimethylocta-2,6-dienyl)cyclohex-2-ene-1,4-dione ***(27)*** *(E : Z mixture).* Pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.54, 1.59, 1.66, 1.68 (each s, total 18H, Me), 1.86–2.12 (m, 14H, ring Me and CH_2), 2.19 (dd, $J = 16$, 8 Hz, 2H, CH_2), 2.41 (dd, $J = 16$, 8 Hz, 2H, CH_2), 2.72 (s, 2H, ring CH_2), 4.90–5.24 (m, 4H, olefinic); IR (neat) 1674 cm^{-1} (C=O); MS (70 eV) m/z 410 (M^+); Anal. Found: C, 81.98; H, 10.60. $C_{28}H_{42}O_2$ calc.: C, 81.90; H, 10.31%. The $E : Z$ ratio was not determined.

Prenylations of haloquinones and hydroxyquinones

These reactions were performed similarly to the allylation of substituted quinones (at -23 °C for 3 h) except for the reactions of 2-methylthio-1,4-naphthoquinone (20 °C, 3 h) and 2-bromo-3-methyl-1,4-naphthoquinone (20 °C, 15 h). Results are shown in Tables 5 and 6.

2-Chloro-3-(3-methylbut-2-enyl)-1,4-naphthoquinone ***(28)***. Yellow crystals; m.p. 93–95 °C (lit. [6c] m.p. 94–96 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.71 (s, 3H, Me), 1.84 (s, 3H, Me), 3.54 (d, $J = 8$ Hz, 2H, CH_2), 5.14 (t, $J = 8$ Hz, 1H, olefinic), 7.78 (m, 2H, Ar), 8.16 (m, 2H, Ar); IR (KBr) 1664 cm^{-1} (C=O).

2-Methyl-3-(3-methylbut-2-enyl)-1,4-naphthoquinone ***(29)*** *[9c].* Yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (s, 3H, Me), 1.82 (s, 3H, Me), 2.20 (s, 3H, ring Me), 3.36 (d, $J = 8$ Hz, 2H, CH_2), 5.06 (t, $J = 8$ Hz, 1H, olefinic), 7.69 (m, 2H, Ar), 8.06 (m, 2H, Ar); IR (neat) 1662 cm^{-1} (C=O).

3-Hydroxy-4-(3-methylbut-2-enylidene)naphthalen-1-one ***(30)***. Yellow crystals; m.p. 148–149 °C (hexane–benzene); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.05 (s, 3H, Me), 2.06 (s, 3H, Me), 6.70 (d, $J = 12$ Hz, 1H, olefinic), 7.02 (s, 1H, OH), 7.40 (s, 1H, ring H), 7.52 (t, $J = 8$ Hz, 1H, Ar), 7.66 (t, $J = 8$ Hz, 1H, Ar), 7.76 (d, $J = 12$ Hz, 1H, olefinic), 8.10 (d, $J = 8$ Hz, 1H, Ar), 8.32 (d, $J = 8$ Hz, 1H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.2 (q), 27.5 (q), 109.6 (d), 121.7 (d), 122.1 (d), 125.1 (s), 126.4 (d), 127.4 (d), 128.7 (s), 130.5 (d), 131.6 (d), 136.1 (s), 147.1 (s), 147.5 (s), 179.4 (s); IR (KBr) 3340 (OH), 1614, 1588 cm^{-1} [–COCH=C(OH)–]; MS (70 eV) m/z 226 (M^+); Anal. Found: C, 79.59; H, 6.19. $C_{15}H_{14}O_2$ calc.: C, 79.62; H, 6.24%.

2,3-Benzo-4,5-dihydroxy-4-(3-phenylprop-2-enyl)cyclohex-5-en-1-one (31). Colourless crystals; m.p. 139–140 °C (benzene); ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.80 (m, 2H, CH_2), 3.80 (d, J = 19 Hz, 1H, ring CH_2), 3.84 (d, J = 19 Hz, 1H, ring CH_2), 4.22 (bs, 1H, OH), 6.12 (dt, J = 16, 7 Hz, 1H, olefinic), 6.40 (d, J = 16 Hz, 1H, olefinic), 7.28 (m, 5H, Ph), 7.30–8.15 (m, 4H, Ar); ^{1}H NMR (90 MHz, CD_3SOCD_3) δ 2.76 (m, 2H, CH_2), 3.34 (br, 1H, OH), 5.60 (s, 1H, ring H), 5.80 (dt, J = 16, 7 Hz, 1H, olefinic), 6.08 (d, J = 16 Hz, 1H, olefinic), 7.20 (m, 5H, Ph), 7.30–7.90 (m, 4H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 48.1 (t), 50.7 (t), 79.8 (s), 121.9 (d), 126.1 (d), 126.2 (d), 127.1 (d), 127.8 (d), 128.5 (d), 129.9 (s), 134.7 (d), 135.4 (d), 136.2 (s). 144.7 (s), 191.5 (s), 203.8 (s); ^{13}C NMR (50 MHz, CD_3OD) δ 49.0 (t), 76.7 (s), 123.9 (d), 125.6 (d), 127.1 (d), 127.3 (d), 128.3 (d), 128.7 (d), 129.4 (d), 130.2 (s), 132.9 (d), 135.1 (d), 138.6 (s), 146.0 (s); C-1, C-2, and C-3 signals were not observed; IR (KBr) 3430 (OH), 1600, 1568, 1500 cm^{-1} [–COCH=C(OH)–]; MS (70 eV) m/z (M^+) calc. 292.1097, obs. 292.1072. Anal. Found: C, 78.14; H, 5.59. $C_{19}H_{16}O_3$ calc.: C, 78.06; H, 5.59. $C_{19}H_{16}O_3$ calc.: C, 78.06; H, 5.52%.

2,3-Benzo-4,5-dihydroxy-6-methyl-4-(3-methylbut-2-enyl)cyclohex-5-en-1-one (32). Pale yellow oil; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.20 (s, 3H, Me), 1.40 (s, 3H, Me), 2.01 (s, 3H, Me), 2.60 (d, J = 8 Hz, 2H, CH_2), 3.01 (bs, 1H, OH), 4.34 (t, J = 8 Hz, 1H, olefinic), 6.60 (s, 1H, OH), 7.20–8.05 (m, 4H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.8 (q), 17.5 (q), 25.7 (q), 40.9 (t), 74.5 (s), 116.6 (d), 125.9 (d), 126.3 (d), 127.8 (d), 128.5 (s), 130.3 (s), 133.1 (d), 136.3 (s), 143.3 (s), 148.3 (s), 179.6 (s); IR (neat) 3410 (OH), 1642, 1602 cm^{-1} [–COCMe=C(OH)–]; MS (70 eV) m/z 189 (M – prenyl). Anal. Found: C, 73.98; H, 7.08. $C_{16}H_{18}O_3$ calc.: C, 74.40; H, 7.02%.

2-(3-Methylbut-2-enyl)-3-methoxy-1,4-naphthoquinone (33) [9c]. Yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.70 (s, 3H, Me), 1.80 (s, 3H, Me), 3.32 (d, J = 8 Hz, 2H, CH_2), 4.14 (s, 3H, OMe), 5.16 (t, J = 8 Hz, 1H, olefinic), 7.72 (m, 2H, Ar), 8.08 (m, 2H, Ar); IR (neat) 1666 cm^{-1} (C=O).

2,3-Benzo-4-(3-methylbut-2-enyl)-4-hydroxy-5-methoxycyclohex-5-en-1-one (34). Colourless crystals; m.p. 110–111 °C (hexane–$CHCl_3$) (lit. [9c] m.p. 131–132 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (s, 3H, Me), 1.56 (s, 3H, Me), 2.67 (m, 2H, CH_2), 2.90 (bs, 1H, OH), 3.66 (s, 3H, OMe), 4.78 (t, J = 8 Hz, 1H, CH_2), 5.88 (s, 1H, ring H), 7.42 (t, J = 8 Hz, 1H, Ar), 7.62 (t, J = 8 Hz, 1H, Ar), 7.78 (d, J = 8 Hz, 1H, Ar), 8.09 (d, J = 8 Hz, 1H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.8 (q), 25.7 (q), 43.2 (t), 55.0 (q), 72.4 (s), 117.2 (d), 118.7 (d), 125.9 (d), 126.7 (d), 128.0 (d), 129.9 (s), 133.1 (d), 136.7 (s), 146.3 (s), 150.1 (s), 181.5 (s); IR (KBr) 3475 (OH), 1660 cm^{-1} (C=O); Anal. Found: C, 73.97; H, 7.04. $C_{16}H_{18}O_3$ calc.: C, 74.40; H, 7.02%.

References

1 (a) R.A. Morton (Ed.), Biochemistry of Quinones, Academic Press, New York, 1965; (b) S. Patai (Ed.), The Chemistry of Quinoid Compounds, Parts 1 and 2, Wiley, New York, 1974; (c) R.H. Thomson, Naturally Occurring Quinones, 3rd ed., Academic Press, New York, 1987.

2 (a) L.F. Fieser, J. Am. Chem. Soc., 61 (1939) 3467; (b) M. Tishler, L.F. Fieser and N.L. Wendler, J. Am. Chem. Soc., 62 (1940) 1982; (c) A.A. Klose and H.J. Almquist, J. Biol. Chem., 132 (1940) 469; (d) R. Hirschmann, R. Miller and N.L. Wendler, J. Am. Chem. Soc., 76 (1954) 4592; (e) O. Isler and K. Doebel, Helv. Chim. Acta, 37 (1954) 225; (f) O. Isler, R. Ruege, L. Chopard-dit-Jean, A. Winterstein and O. Wiss, Helv. Chim. Acta, 41 (1958) 786; (g) C.H. Shunk, B.O. Linn, E.L. Wong, P.E. Wittreich and F.M. Robinson, J. Am. Chem. Soc., 80 (1958) 4753; (h) C.H. Shunk, R.E.

Erickson, E.L. Wong and K. Folkers, J. Am. Chem. Soc., 81 (1959) 5000; (i) N. Trenner, B.H. Arison, R.E. Erickson, C.H. Shunk, D.E. Wolf and K. Folkers, J. Am. Chem. Soc., 81 (1959) 2026; (j) V. Glorr, O. Isler, R.A. Morton, R. Ruegg and O. Wiss, Helv. Chim. Acta, 41 (1958) 2357.

3 (a) C.D. Snyder and H. Rapoport, J. Am. Chem. Soc., 96 (1974) 8046; (b) R.W. Raynolds, M.J. Manning and J.S. Swenton, J. Chem. Soc., Chem. Commun., (1977) 499; (c) L. Syper, K. Kloc and J. Mlochowski, Tetrahedron, 36 (1980) 123; (d) Y. Fujita, M. Ishiguro, T. Onishi and T. Nishida, Synthesis, (1981) 469; (d) S. Araki, T. Sato, H. Miyagawa and Y. Butsugan, Bull. Chem. Soc. Jpn., 57 (1984) 3523.

4 (a) K. Saito, S. Inoue and R. Yamagichim J. Org. Chem., 37 (1972) 1889; (b) L.S. Hegedus, E.L. Waterman and J. Catline, J. Am. Chem. Soc., 94 (1972) 7155; (c) K. Sato, S. Inoue and K. Saito, J. Chem. Soc., Chem. Commun., (1972) 953; J. Chem. Soc., Perkin Trans., 1 (1973) 2289; (d) S. Inoue, R. Yamagami and K. Saito, Bull. Chem. Soc. Jpn., 47 (1974) 3098.

5 (a) C. Blomberg, H.H. Grootveld, T.H. Gerner and F. Bickelhaupt, J. Organomet. Chem., 23 (1970) 549; (b) A. Fischer and G.N. Henderson, Tetrahedron Lett., (1980) 701, and references cited therein; (c) D.A. Evans and J.M. Hoffmann, J. Am. Chem. Soc., 98 (1976) 1983.

6 (a) H. Sugihara, Y. Kawamatsu and H. Morimoto, Justus Liebigs Ann. Chem., 763 (1972) 128; (b) Y. Tachibana, Chem. Lett., (1977) 901; (c) N.K. Kapoor, R.B. Gupta and R.N. Khanna, Indian J. Chem., Sect. B, 21B (1982) 189.

7 (a) L.S. Hegedus, S.D. Wagner, E.L. Waterman and K. Siirala-Hansen, J. Org. Chem., 40 (1975) 593; (b) L.S. Hegedus, B.R. Evans, D.E. Korte, E.L. Waterman and K. Sjoberg, J. Am. Chem. Soc., 98 (1976) 3901; (c) L.S. Hegedus and B.R. Evans, J. Am. Chem. Soc., 100 (1978) 3461.

8 A. Hosomi and H. Sakurai, Tetrahedron Lett., (1977) 4041.

9 (a) K. Maruyama and Y. Naruta, J. Org. Chem., 43 (1978) 3796; (b) Y. Naruta and K. Maruyama, Chem. Lett., (1979) 881, 885; (c) Y. Naruta, J. Am. Chem. Soc., 102 (1980) 3774; (d) Y. Naruta, J. Org. Chem., 45 (1980) 4097; (e) A. Takuwa, O. Soga, T. Mishima and K. Maruyama, J. Org. Chem., 52 (1987) 1261.

10 (a) S. Araki, H. Ito and Y. Butsugan, J. Org. Chem., 53 (1988) 1831; (b) S. Araki, T. Shimizu, P.S. Johar, S.-J. Jin and Y. Butsugan, J. Org. Chem., 56 (1991) 2538.

11 S. Araki, N. Katsumura, H. Ito and Y. Butsugan, Tetrahedron Lett., 30 (1989) 1581.

12 (a) A.R. Burnett and R.H. Thomson, J. Chem. Soc. (C), (1967) 2100; (b) W. Sandermann and M.H. Simatupang, Chem. Ber., 96 (1963) 2182; (c) H.H. Dietrichs, Naturwissenschaften, 51 (1964) 408.

13 B.M. Mikhailov, G.S. Ter-Sarkisyan and N.A. Nikolaeva, Izv. Akad. Nauk. SSSR, Ser. Khim., 3 (1968) 541.

14 G.S. Ter-Sarkisyan, N.A. Nikolaeva, V.G. Kiselev and B.M. Mikahilov, Zh. Obshch. Khim., 41 (1971) 152.

15 K.H. Dotz and I. Pruskil, Chem. Ber., 113 (1980) 2876.

16 R.J. Deshpande, Indian J. Chem., Sect. B, 16B (1978) 389.

17 A. Cheung, J.W. Suttie, BioFactors, 1 (1988) 61.