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Chemoselective method for the synthesis of 4-allyl-4-hydroxycyclohexa-2,5-dienone derivatives from 1,4-quinones by an indium-mediated allylation protocol

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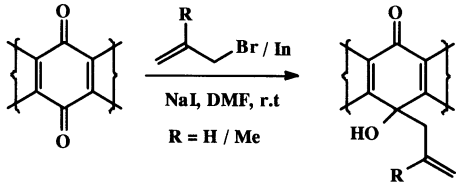
Abstract—Allyl indium halide on reaction with 1,4-quinones produced 4-allyl-4-hydroxycyclohexa-2,5-dienone derivatives. Unsymmetrical quinones show high chemoselectivity in addition of allyl indium halide reagent to the carbonyl group.

The use of allyl indium halides[1] as organometallic reagents for the allyl group transfer has gained importance in the last few years due to its generality, mild, easy and high yielding reaction conditions. Various homoallylic alcohols[2,3] homoallylvinylcyclopropanes[4] and *gem* diallylbutenolides/phthalides[5] have been synthesised by reaction of such reagents with suitable aldehydes/ketones,[2] hydrazones,[6] azetidinones,[7] epoxides,[8] acid anhydrides[5] etc. In connection with our studies toward the preparation of sol–gel glass[9] through polymerisation of triethoxysilane derivatives of polyarenes we were in need of some polyallylated polyarene systems, which can easily be converted to the triethoxysilane derivatives via hydrosilylation with $(EtO)_3SiH$ and Spier's catalyst (Fig. 1).[10]

Though the reaction of allyl indium halide with 1,2-or 1,3 diketones[11,12] are known, to the best of our knowledge, there are two reports[13a,b] on studies of the reaction of allyl indium halides with 1,4-diketones or 1,4 benzoquinone derivative only. However there is a report on allylation of 1,4-quinones using Cd as catalyst.[13c] Here we report our results on the synthesis of some 4-allyl-4-hydroxycyclohexa-2,5-dienone derivatives by reaction of suitable 1,4-quinone derivatives with allyl indium iodides (Scheme 1). Thus 1,2-dihydroxy-9,10-anthraquinone (alizarin) (**1**) (1 equiv.) was treated with allylindium iodide generated in situ by reaction with indium metal (1.05 equiv.) and allyl bromide (1.55 equiv.) in the presence of NaI (1.55 equiv.) in DMF (3 mL) to furnish 10-allyl-3,4,10-trihydroxy-10*H*-anthracen-9-one (**6**) in 71% yield. (Table 1, entry 1) Out of the two carbonyl groups only one was found to react with the reagent while the other remained unaffected despite the use of excess of reagents. Similarly compound **2** under the said reaction condition



Scheme 1.

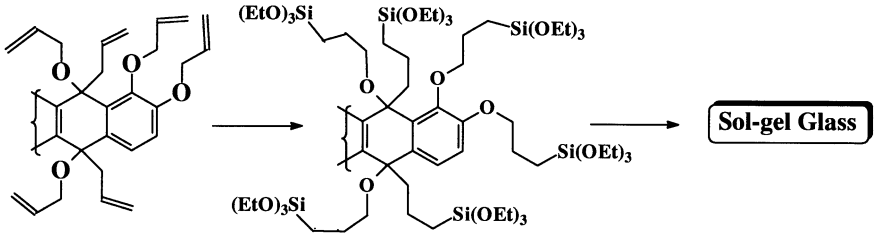


Figure 1.

Keywords: 1,4-quinone derivatives; allyl indium halide; allylation; chemoselective addition; 2,5-cyclohexadienones.
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Table 1. Allylation of anthraquinone derivatives

Entry	Anthraquinone derivative	Product (yield %)[a]
1	**1**	**6** (71)
2	**2**	**7** (66)
3	**3**	**8** (61)
4	**4**	**9** (70)
5	**5**	**10** (68)

[a] Isolated yield.

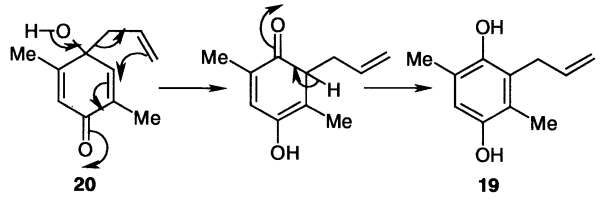
However the reactions of 1,4-benzoquinones or 1,4-naphthoquinones with allylindium reagents were not so smooth and non-uniform results were obtained depending on the substrate and reaction conditions employed (Figure 4) (Table 2).

Thus, reactions of *p*-benzoquinone (**11**) with allylindium iodide at room temperature or at −23°C afforded no cyclohexadienone derivatives but the 2-allylhydroquinone **18** as the only isolable product (Table 2, entry 6) whereas its

Table 2. Allylation of 1,4-benzoquinone and 1,4-naphthoquinone derivatives

Entry	1,4-Benzo-/naphthoquinone derivatives	Product (yield)	
		Room temperature	−23°C
6	**11**	**18**+other products (72%)	**18** (73%)
7	**12**	**19** (69%)	**20** (61%)
8	**13**	–	**21** (74%)
9	**14**	**22** (50%)	**22** (59%)
10	**15**	**23** (69%)	**24** (51%)
11	**15**	**25** (63%)	–
12	**16**	**26**+**27** (73%) (1.6:1)	**26**+**27** (73%) (1.6:1)
13	**17**	–	**28**+**29** (73%) (1:1.4)

afforded **7** as a white solid in very good yield (entry 2). Other 1,4-quinone derivatives also behaved in a similar way (Figure 3) (entries 3,4 and entry 5) where 2-methyl allylindium halide was used for allylation. In the case of unsymmetrical quinones high chemoselectivity was observed towards the addition of the reagent on the carbonyl group in close proximity to the OH/OR group (entries 1–4). This is probably due to the participation of the lone pair of electrons of oxygen in coordination with the reagent. The reactions were very clean and produced the desired product in high yield. The results are summarised in Table 1.



Scheme 2.

2,5-dimethyl analogue (**12**) under identical conditions produced 4-allyl-4-hydroxy-2,5-dimethylcyclohex-2,5-dienone (**20**), at −23°C and the product formed at room temperature was found to be the hydroquinone derivative **19** (entry 7). Compound **19** is possibly formed via rearrangement of **20** as indicated by the fact that when pure **20** is stirred at room temperature with SiO_2 in chloroform, it is converted to **19**. A possible pathway for such conversion may be as in Scheme 2.

In entry 6, use of low temperature furnished a cleaner product in high yield whereas the reaction at room temperature furnished **18** along with some unidentified side products in very minor amounts.

In the case of compound **13** the addition was found to be directed by the presence of the heteroatom at 2-position of the carbonyl moiety. Thus compound **13**, on treatment with allyl bromide/In/NaI in DMF at −23°C produced **21** as the only isolable product in 74% yield where the allyl group reacted with the C_1-carbonyl group adjacent to the SPh

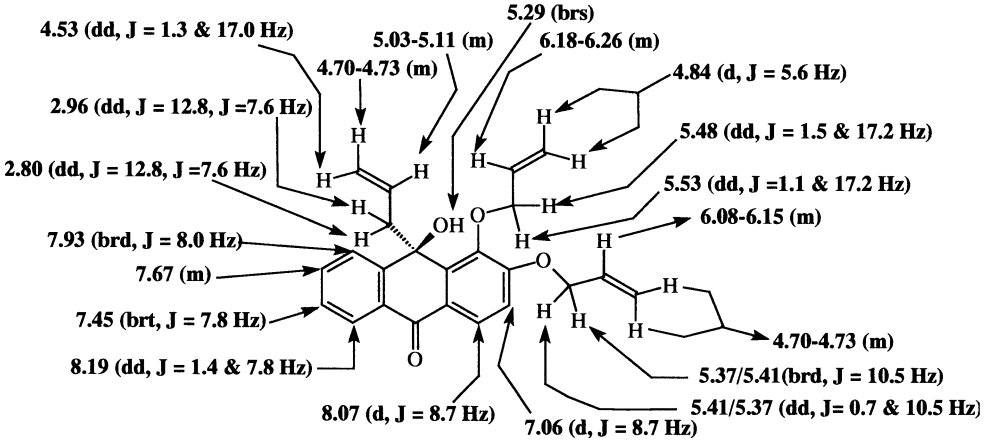


Figure 2. Representative ^{1}H NMR data of compound **9**.

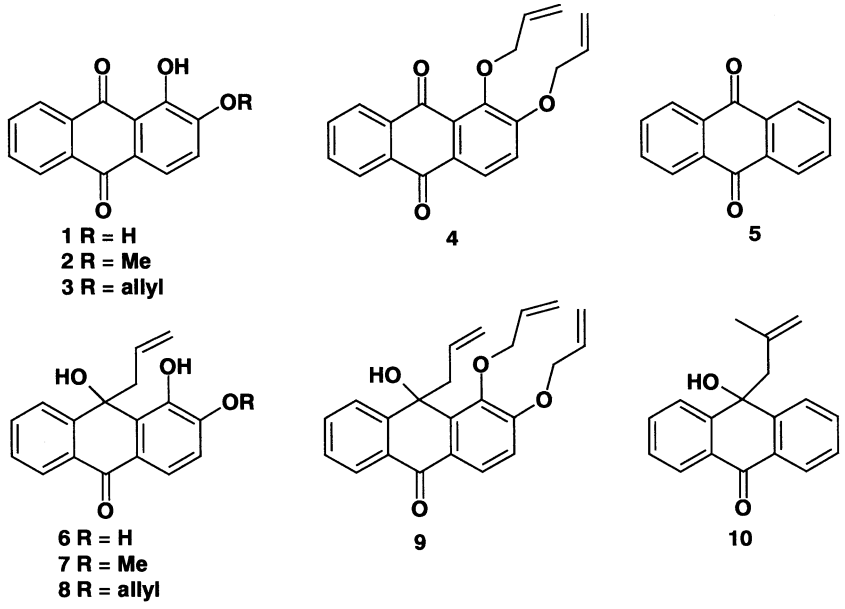


Figure 3.

moiety and the other carbonyl moiety C_4 remained unaffected (entry 8). Compound **14** also reacted in a similar fashion to furnish compound **22** as the only isolable product both at room temperature and at −23°C, however the yield at −23°C was better (~59%) compared to that at room temperature (50%) (entry 9). In the case of 1,4-naphthoquinones such as compound **15**, allylation (at room temperature) with allyl/2-methylallyl indium halides furnished 4-hydroxycyclohexadienone derivatives **23** and **25**, respectively, while the reaction of allyl indium halide with **15** at

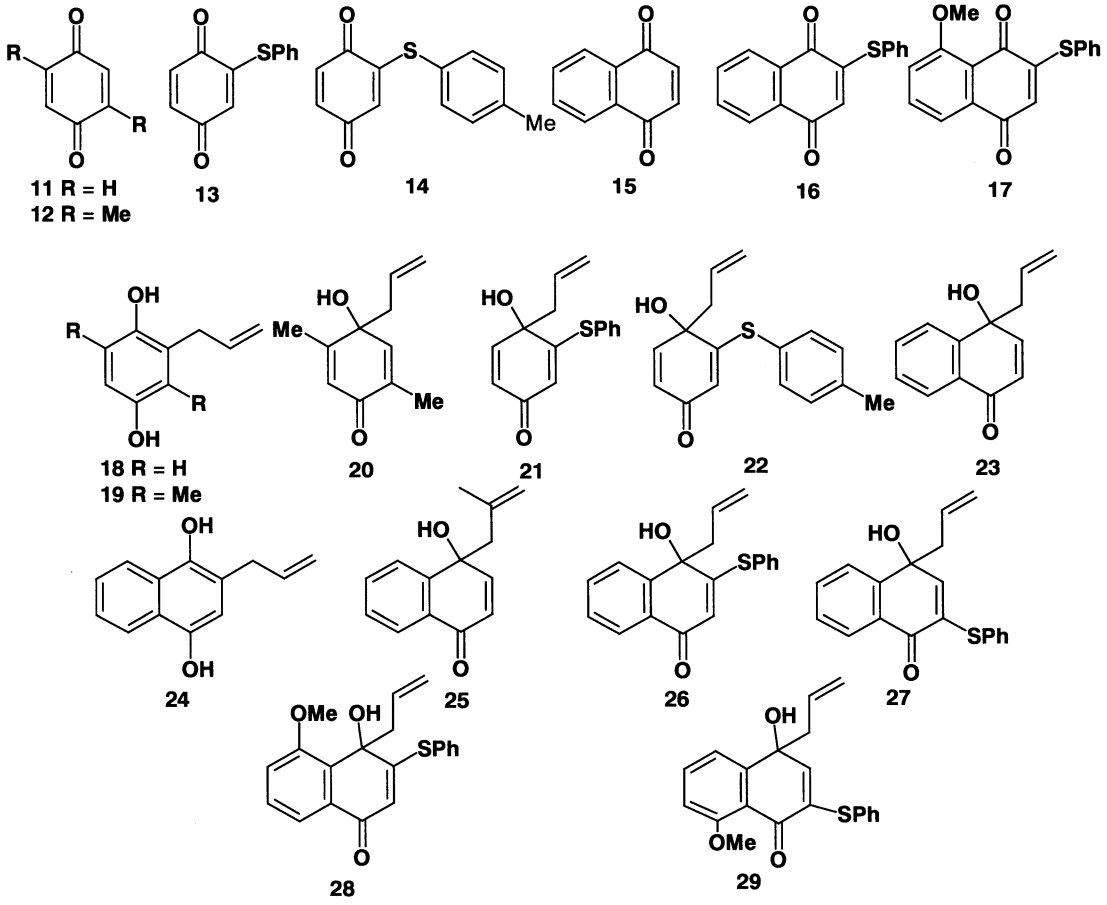


Figure 4.

−23°C produced 2-allyl-1,4-dihydroxynaphthalene (**24**) as the only product in 51% yield (entries 10 and 11). In the case of **16** or **17** the reaction was found to be less chemoselective due to the increased peri interaction. Thus compound **16** on reaction with allylbromide/In/NaI in DMF at −23°C and at room temperature produced a mixture of **26** and **27** in the ratio 1.6:1. Here the major product **26** resulted through the allylation of the C_1 carbonyl assisted by −SPh participation with the allyl indium reagent (entry 12). Interestingly, the ratio of products **28** and **29** formed from allylation of 8-methoxy-2-phenylsulfanyl-1,4-naphthoquinone (**17**) was just the reverse of the above result (entry 13). Here, to the presence of an extra methoxy group at position 8 of the naphthoquinone moiety further increased the *peri* interaction at the C_1 carbonyl.

Thus despite the co-ordination of −SPh group with the reagent the steric factors controlled the product and it is the less hindered carbonyl group at C_4 that reacted in preference over the other carbonyl group to form a mixture of **28** and **29** in the ratio of 1:1.4 in the reaction mixture (entry 13) (ratio of the products in each case was determined from the ^{1}H NMR spectra).

The results are summarised in Table 2. The compounds were characterised by usual spectroscopic methods and analysis. A representative ^{1}H NMR data of compound **9** is shown in Fig. 2. Thus we describe a high yielding general method for the synthesis of 4-hydroxy-4-allylcyclohexa-2,5-dienone derivatives of 1,4-quinones by an indium mediated allylation protocol (Figs. 3 and 4).

1. Experimental

1.1. General

All melting points are uncorrected and recorded in one-side open glass capillaries using a sulfuric acid bath. Dimethyl formamide was dried and distilled prior to use according to the standard procedure. Indium metal was purchased from SRL India Ltd. NMR spectra were recorded on 200 or 500 MHz Bruker spectrometer in $CDCl_3$ (dried with 4 Å molecular sieves) as solvent. Coupling constant (J) values are given in Hz. IR spectra were recorded on a Perkin–Elmer 800 machine. Elemental values were obtained from CDRI, Lucknow. TLC was performed on pre-coated silica gel plates (Fluka). Yields of the products refer to spectroscopically homogenous substances.

1.2. General method for the synthesis of 4-hydroxy-4-allyl cyclohexa-2,5-dienone derivatives

To a stirred suspension of In-metal (1.05 mmol) and sodium iodide (1.55 mmol), in dry DMF (2–3 mL) at room temperature allyl bromide (or 2-methyl allyl bromide) (1.55 mmol) was added dropwise. The stirring was continued at room temperature until all the indium metal dissolved. To this a solution of 1,4-quinone derivatives in DMF (1–2 mL) was added dropwise and stirred further for 3–5 h (completion of the reaction was checked by TLC). The reaction mixture was quenched with a few drops of dil HCl and diluted with water. It was then extracted with ethyl acetate and the organic layer was thoroughly washed with water and dried (Na_2SO_4). Removal of solvent under reduced pressure followed by purification of the residue obtained furnished the 4-hydroxy-4-allyl cyclohexa-2,5-dienone derivatives or the hydroquinone derivatives in 35–74% yield.

1.2.1. 10-Allyl-3,4,10-trihydroxy-10*H*-anthracen-9-one (6). Yellow solid, mp 152–154°C ($CHCl_3$–petroleum ether 60–80°C), yield 71%; IR (KBr) ν_{max} 3199 (br), 3303 (br), 3393 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.74 (dd, 1H, J=7.4, 12.8 Hz), 2.99 (dd, 1H, J=7.2, 12.8 Hz), 3.25–4.10 (br, 1H, exchangeable with D_2O), 4.58 (brd, 1H, J=16.8 Hz), 4.76 (dd, 1H, J=1.8, 10.1 Hz), 4.95–5.12 (m, 1H), 6.10–6.40 (br, 1H, exchangeable with D_2O), 6.95 (d, 1H, J=8.5 Hz), 7.39–7.47 (m, 1H), 7.60–7.68 (m, 1H), 7.66 (d, 1H, J=8.5 Hz), 7.78 (d, 1H, J=7.7 Hz), 8.07 (d, 1H, J=7.8 Hz), 8.91 (brs, 1H, exchangeable with D_2O); ^{13}C NMR ($CDCl_3$) δ 48.45, 75.99, 115.21, 120.51, 121.27, 124.73, 127.03, 128.57, 129.50, 130.58, 133.31, 141.30, 144.62, 150.07, 180.39. Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96. Found: C, 72.05; H, 4.78.

1.2.2. 10-Allyl-4,10-dihydroxy-3-methoxy-10*H*-anthracen-9-one (7). Yellow viscous liquid, yield 66%; IR (KBr) ν_{max} 1642, 3387 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.70 (dd, 1H, J=7.3, 12.7 Hz), 3.00 (dd, 1H, J=7.4, 12.7 Hz), 3.88 (s, 3H), 4.44–4.70 (m, 2H), 4.80 (brs, 1H), 4.92–5.06 (m, 1H), 6.87 (d, 1H, J=8.7 Hz), 7.38–7.46 (m, 1H), 7.57–7.66 (m, 2H), 7.73 (d, 1H, J=8.7 Hz), 7.81 (brd, 1H, J=7.7 Hz), 8.09 (dd, 1H, J=1.3, 7.8 Hz). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.97; H, 5.40. Found: C, 72.68; H, 5.15.

1.2.3. 10-Allyl-3-allyloxy-4,10-dihydroxy-10*H*-anthracen-9-one (8). Yellow oil (column chromatography, CH_2Cl_2–ether=8:2), yield 61%; IR (KBr) ν_{max} 1639, 3199 (br), 3393 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.71 (brs, 1H), 2.77 (dd, 1H, J=7.3, 12.7 Hz), 3.12 (dd, 1H, J=7.3, 12.7 Hz), 4.49–4.81 (m, 4H), 4.94–5.11 (m, 1H), 5.35–5.51 (m, 2H), 6.04–6.12 (m, 1H), 6.98 (d, 1H, J=8.6 Hz), 7.34 (brs, 1H), 7.42–7.49 (m, 1H), 7.61–7.69 (m, 1H), 7.83 (d, 1H, J=8.6 Hz), 7.86 (brd, 1H, J=7.9 Hz), 8.17 (brd, 1H, J=7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 49.47, 69.86, 73.71, 111.63, 119.02, 119.43, 120.60, 124.90, 125.52, 126.49, 127.84, 130.17, 130.48, 131.30, 132.02, 133.14, 142.52, 145.29, 149.84, 182.39. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.53; H, 5.59. Found: C, 74.24; H, 5.41.

1.2.4. 10-Allyl-3,4-bis-allyloxy-10-hydroxy-10*H*-anthracen-9-one (9). Yellow oil (column chromatography, CH_2Cl_2–ether=8:2), yield 70%; IR (KBr) ν_{max} 1661, 3429 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.80 (dd, 1H, J=7.6, 12.8 Hz), 2.96 (dd, 1H, J=7.6, 12.8 Hz), 4.53 (dd, 1H, J=1.3, 17.0 Hz), 4.70–4.73 (m, 3H), 4.84 (d, 2H, J=5.6 Hz), 5.03–5.11 (m, 1H), 5.29 (brs, 1H, exchangeable with D_2O), 5.37 (dd, 1H, J=0.7, 10.5 Hz), 5.41 (brd, 1H, J=10.5 Hz), 5.48 (dd, 1H, J=1.5, 17.2 Hz), 5.53 (dd, 1H, J=1.1, 17.2 Hz), 6.08–6.15 (m, 1H), 6.18–6.26 (m, 1H), 7.06 (d, 1H, J=8.7 Hz), 7.45 (brt, 1H, J=7.8 Hz), 7.67 (m, 1H), 7.93 (brd, 1H, J=8.0 Hz), 8.07 (d, 1H, J=8.7 Hz), 8.19 (dd, 1H, J=1.4, 7.8 Hz). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.24; H, 6.08. Found: C, 76.08; H, 5.89.

1.2.5. 10-Hydroxy-10-(2-methyl-allyl)-10*H*-anthracen-9-one (10). White solid, mp 116–118°C ($CHCl_3$–petroleum ether 60–80°C), yield 68%; IR (KBr) ν_{max} 1658, 3490 (brs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (d, 3H, J=1.0 Hz), 2.69 (s, 3H), 3.86 (brs, 1H), 4.56 (m, 1H), 7.43–7.51 (m, 2H), 7.62–7.70 (m, 2H), 7.93 (brd, 2H, J=7.3 Hz), 8.18 (dd, 2H, J=1.4, 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 23.68, 56.62, 73.14, 117.03, 125.97, 128.89, 128.12, 131.38, 133.26, 139.26, 139.33, 147.02, 180.11. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.81; H, 6.06. Found: C, 81.63; H, 5.84.

1.2.6. 2-Allyl-benzene-1,4-diol (18). White solid, mp 90–92°C ($CHCl_3$–petroleum ether 60–80°C), (Literature mp 93°C),[14] yield 73%; IR (KBr) ν_{max} 3460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.33 (d, 2H, J=6.3 Hz), 4.41 (brs, 1H), 4.35 (brs, 1H), 5.09–5.18 (m, 2H), 5.90–6.10 (m, 1H), 6.57–6.75 (m, 3H).

1.2.7. 3-Allyl-2,5-dimethyl-benzene-1,4-diol (19). White solid, mp 138–140°C ($CHCl_3$–petroleum ether 60–80°C), (Literature mp 141–142°C),[15] yield 69%; ^1H NMR ($CDCl_3$) δ 2.15 (s, 3H), 2.18 (s, 3H), 3.41–3.45 (m, 2H), 4.35 (brs, 1H, exchangeable with D_2O), 4.41 (brs, 1H, exchangeable with D_2O), 4.96–5.10 (m, 2H), 5.85–6.02 (m, 1H), 6.50 (s, 1H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 73.87; H, 7.59.

1.2.8. 4-Allyl-4-hydroxy-2,5-dimethyl-cyclohexa-2,5-dienone (20). Pale yellow solid, mp 56–58°C (Literature mp 60°C),[13a] yield 61%; ^1H NMR ($CDCl_3$) δ 1.77 (d, 3H, J=1.3 Hz), 1.97 (d, 3H, 1.25 Hz), 2.45 (d, 2H, J=7 Hz), 3.27 (brs, 1H), 4.96–5.10 (m, 2H), 5.27–5.48 (m, 1H), 5.89 (d, 1H, J=1.3 Hz), 6.53 (d, 1H, J=1.4 Hz).

1.2.9. 4-Allyl-4-hydroxy-3-phenylsulfanylcyclohexa-2,5-dienone (21). Viscous oil (column chromatography, CH_2Cl_2–ether=8:2), yield 74%; IR (KBr) ν_{max} 1652, 3520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52 (brs, 1H), 2.76–2.83 (m, 2H), 5.13–5.27 (m, 2H), 5.50–5.55 (m, 2H), 6.16 (dd, 1H, J=1.4, 9.8 Hz), 6.82 (d, 1H, J=9.9 Hz), 7.45–7.48 (m, 5H). Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.77; H, 5.43. Found: C, 69.52; H, 5.12.

1.2.10. 4-Allyl-4-hydroxy-3-*p*-tolylsulfanylcyclohexa-2,5-dienone (22). White solid; mp 110–112°C ($CHCl_3$–petroleum ether 60–80°C), yield 59%; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.51 (brs, 1H), 2.77 (m, 2H), 5.11–5.25 (m, 2H), 5.48 (d, 1H, J=1.7 Hz), 5.49–5.59 (m, 1H), 6.14 (dd, 1H, J=1.8, 9.8 Hz), 6.79 (d, 1H, J=10.1 Hz), 7.22–7.37 (m, 4H). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.59; H, 5.88. Found: C, 70.31; H, 5.62.

1.2.11. 4-Allyl-4-hydroxy-4*H*-naphthalen-1-one (23). White solid, mp 78–80°C, ($CHCl_3$–petroleum ether 60–80°C) (literature mp 81–82°C)[16] yield 69%; IR (KBr) ν_{max} 1678, 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (brs, 1H), 2.64–2.69 (m, 2H), 4.88–5.03 (m, 2H), 5.35–5.45 (m, 1H), 6.31 (d, 1H, J=10.3 Hz), 6.93 (d, 1H, J=10.3 Hz), 7.37–7.45 (m, 1H), 7.56–7.67 (m, 1H), 7.72 (dd, 1H, J=1.2, 7.8 Hz), 8.01 (dd, 1H, J=1.2, 7.8 Hz). Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Found: C, 77.78; H, 5.78.

1.2.12. 2-Allyl-naphthalene-1,4-diol (24). Yellow solid, mp 136–138°C, ($CHCl_3$–petroleum ether 60–80°C) (literature mp 142–143°C)[16] yield 51%; 3.48–3.52 (m, 2H), 5.08–5.27 (m, 2H), 4.9–5.3 (br, 2H), 5.95–6.11 (m, 1H), 6.61 (s, 1H), 7.45–7.55 (m, 2H), 8.05–8.15 (m, 2H).

1.2.13. 4-Hydroxy-4-(2-methyl-allyl)-4*H*-naphthalen-1-one (25). White solid, mp 81–83°C, ($CHCl_3$–petroleum ether 60–80°C), yield 63%; IR (KBr) ν_{max} 1648, 3375 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 3H), 1.67 (brs, 1H), 2.55–2.76 (m, 2H), 4.52–4.53 (m, 1H), 4.80–4.83 (m, 1H), 6.32 (d, 1H, J=10.3 Hz), 6.97 (d, 1H, J=10.3 Hz), 7.38–7.46 (m, 1H), 7.58–7.66 (m, 1H), 7.76 (dd, 1H, J=1.2, 7.7 Hz), 8.03 (dd, 1H, J=1.3, 7.8 Hz). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.27; H, 6.28.

1.2.14. 4-Allyl-4-hydroxy-3-phenylsulfanyl-4*H*-naphthalen-1-one (26). (Isolated), yellow viscous oil (column chromatography, CH_2Cl_2–ether=8:2), yield 35%; IR (KBr) ν_{max} 1659, 3376 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (brs, 1H, OH), 2.87 (dd, 1H, J=7.7, 12.9 Hz), 3.04 (dd, 1H, J=7.8, 12.8 Hz), 4.86–4.98 (m, 2H), 5.05–5.30 (m, 1H), 5.72 (s, 1H), 7.38–7.57 (m, 6H), 7.57–7.65 (m, 1H), 7.78 (dd, 1H, J=1.1, 7.9 Hz), 8.05 (dd, 1H, J=1.3, 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 50.15, 74.87, 119.96, 121.52, 125.27, 126.03, 127.99, 128.11, 130.06, 130.15, 130.46, 132.29, 135.89, 145.69, 180.89. Anal. Calcd for $C_{19}H_{16}O_2S$: C, 74.03; H, 5.19. Found: C, 73.82; H, 4.86.

1.2.15. 4-Allyl-4-hydroxy-3-phenylsulfanyl-4*H*-naphthalen-1-one (26) and 4-allyl-4-hydroxy-2-phenylsulfanyl-4*H*-naphthalen-1-one (27). (Mixture, ratio 1.6:1, as indicated from ^1H NMR, when the reaction was carried out at −23°C), yellow oil, yield 73%; ^1H NMR ($CDCl_3$) δ 2.55 (brd, J=7.3 Hz, allylic CH_2 of **27**), 2.8 (m) and 3.05 (m) (allylic CH_2 of **26**), 4.81–4.98 (m, vinylic CH_2), 5.05–5.9 (m, vinylic CH), 5.66 (s) and 6.11 (s) (H^3 and H^2 of **27** and **26**, respectively), 7.35–7.77 (aromatic), 7.75 (dd, J=1.1, 7.8 Hz), 8.05 (dd, J=1.4, 7.7 Hz) (aromatic).

1.2.16. 4-Allyl-4-hydroxy-5-methoxy-3-phenylsulfanyl-4*H*-naphthalen-1-one (28) and 4-allyl-4-hydroxy-8-methoxy-2-phenylsulfanyl-4*H*-naphthalen-1-one (29). (Mixture, ratio 1:1.4 as indicated from ^1H NMR), yellow oil, yield 73%; ^1H NMR ($CDCl_3$) δ 2.52 (brd, J=7.3 Hz, allylic CH_2 of minor isomer **28**), 3.05–3.25 (m, allylic CH_2 of **29**), 3.95 (s, OCH_3 of **28**), 4.03 (s, OCH_3 of **29**), 4.85–5.1 (m, vinylic CH_2), 5.10–5.4 (m, vinylic CH), 5.15 (s, OH, exchangeable with D_2O), 5.73 (s, H^3 of major isomer **29**), 5.96 (s, H^2 of minor isomer **28**), 6.95 (brd, J=8.3, H^6 of minor isomer **28**), 7.15 (brd, J=7.4 Hz, H^7 of major isomer 29), 7.18–7.56 (m, aromatic), 7.75 (brd, H^8 of minor isomer **28**).

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