

Vijay Nair* and Sasi Kumar

Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum-695 019, India

The reactions of 3,5-di-*tert*-butyl-, 4-*tert*-butyl- and 3-methoxy-*o*-benzoquinones with various acyclic dienes have been studied. Very efficient formation of benzodioxine adducts was observed in a number of cases.

Introduction

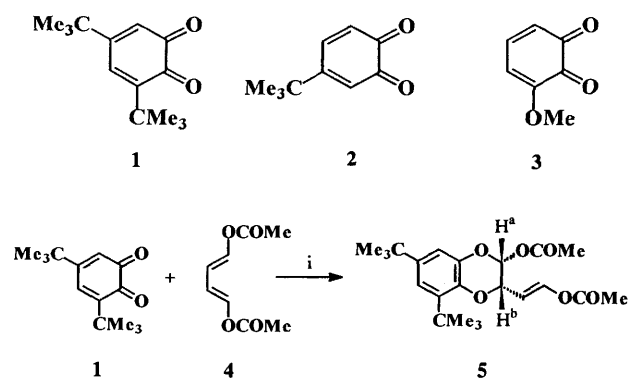
Quinones are versatile organic compounds endowed with rich and fascinating chemistry. Quite often they serve as versatile intermediates in organic synthesis and in the dye industry. They play a vital role in electron transport in the respiratory and photosynthetic elements of biological systems as well as a number of redox processes in nature.²

In recent years there has been a great deal of interest in the synthesis of quinonoid natural products and the Diels–Alder reaction has been employed to great advantage. We have been particularly interested in the Diels–Alder chemistry of *o*-benzoquinones because their reactivity profile in cycloaddition reactions is quite interesting. Potentially they can function as carbodienes, heterodienes or dienophiles in Diels–Alder reactions.^{3–15} The dienophilic activity of *o*-benzoquinones has been exploited in many natural-product syntheses.^{16–20} Diels–Alder reactions of acyclic dienes with *o*-benzoquinone and mono-, di-, and tri-substituted *o*-benzoquinones have been studied by Ansell *et al.*³ in 1971. In these reactions the quinone always acts as a dienophile, with the addition occurring preferentially to the more electron-deficient olefinic linkage. In some cases the adducts are labile and the primary products are not isolable. Simple *o*-benzoquinones are unstable compounds and they undergo rapid dimerization. Therefore the cycloadditions with acyclic dienes proceed in low yield. Ansell *et al.* have used a large excess of the diene in order to circumvent the dimerization.⁴ The reactions of monomethyl-, methoxy-, chloro- and acetamido-*o*-benzoquinones were comparable to those of benzoquinone itself. In all cases addition occurred at the less hindered double bond. Danishefsky *et al.* have reported unusual solvent effects noticed during the cycloaddition process.^{10–12} In spite of the above investigations, much remains to be learned about the reactivity profile of *o*-quinones in cycloadditions and therefore we have undertaken some work in this area. We were particularly interested in understanding the course of the Diels–Alder reaction between *o*-quinones and electron-rich dienes. Such reactions have not been exploited previously. The results of our investigations in this area are reported here.

Results and discussion

The focus of our attention has been the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone **1**, 4-*tert*-butyl-*o*-benzoquinone **2** and 3-methoxy-*o*-benzoquinone **3** with various acyclic dienes such as 1,4-diacetoxybuta-1,3-diene, 1-acetoxyhexa-2,4-diene, 2,5-dimethylhexa-2,4-diene, (*E,E*)-dimethylocta-2,4,6-triene, 2,3-dimethylbuta-1,3-diene, etc.

3,5-Di-*tert*-butyl-*o*-benzoquinone **1** on treatment with 1,4-diacetoxybuta-1,3-diene **4** in toluene in a sealed tube (120 °C) afforded a product in 90% yield. This was characterized as the benzodioxine **5**. The reaction can be illustrated as Scheme 1.



Scheme 1 Reagents and conditions: i, Toluene, sealed tube, 120 °C, 30 h (90%)

The IR spectrum of **5** shows a strong absorption at 1770 cm⁻¹ due to the presence of acetate groups. In the ¹H NMR spectrum of **5** two tertiary butyl resonances appeared at δ 1.26 and 1.36 downfield from SiMe₄. The two acetyl groups appeared at δ 2.12. The doublet at δ 6.2 is coupled with the doublet of the proton at δ 4.60. The coupling constant ($J = 3.3$ Hz) for these two protons indicates that they are *cis* to each other. The large coupling constant ($J = 12.5$ Hz) for olefinic protons at δ 5.50 and 7.55 indicates a *trans* (*E*) geometry for the alkene. The signals at δ 6.84 and 6.94 ($J = 2.3$ Hz) are due to the aromatic protons. In the ¹³C NMR spectrum typical carbon signals have been observed for the carbons adjacent to the ring oxygen at δ_c 89.32 and 70.50. The two ester carbonyls resonated at δ_c 167.5 and 169.61. The two acetate carbon (CH₃CO) signals appeared at δ_c 20.58 and 21.08. The two *tert*-butyl carbon signals resonated at δ_c 29.76 and 31.45. The connectivity of the protons in compound **5** has been established by 2D homonuclear chemical-shift correlation spectroscopy (COSY) experiments. From the 2D spectrum it has been found that the proton signal at δ 4.60 is coupled with signals at δ 7.55, and 6.20 and 5.5, thus clearly indicating the connectivity between various protons in compound **5**.

The *cis* disposition of the protons discernible from the *J*-values (3.3 Hz) precludes a concerted addition of 1,4-dioxabutadiene (*o*-quinone carbonyl) with the diene; such a cyclization would lead to a *trans* orientation of the ring junction. The calculated *J*-value (*cis* = 3 Hz, *trans* = 7 Hz, MMX method) is also in agreement with the proposed structure.† The energy-minimized structure is presented in

† The energy-minimization calculation with the PC MODEL was performed for two geometries: (i) with H^a and H^b *cis*, and (ii) with H^a and H^b *trans*. The H–C–C–H dihedral angle for *cis* geometry is $\approx 60^\circ$, while it is $\approx 180^\circ$ for *trans* geometry. Thus, by using the modified Karplus equation ref. 21 the following *J*-values were obtained: *cis*-structure $J_{H-H} \leq 3$ Hz; *trans*-structure $J_{H-H} \geq 7$ Hz.

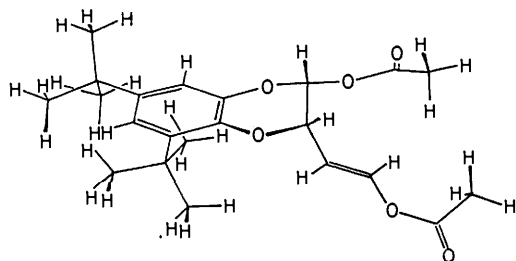
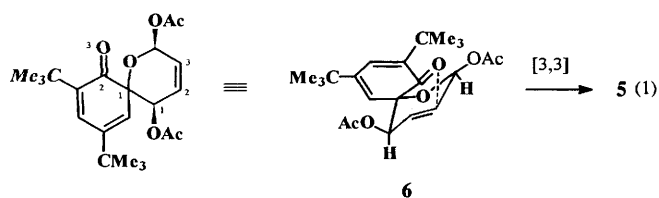
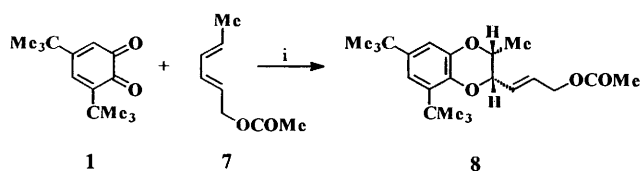


Fig. 1 Energy-minimized structure of compound **5** (MMX method)

Fig. 1. A comparison of the observed J -value (8 Hz) for *trans*-coupled protons in a benzodioxine system reported recently also lends support to the assigned stereochemistry.²² The observed stereochemistry can be accounted for by invoking the following two-step process:† (i) the electron-rich diene participates in a hetero-Diels–Alder reaction with the less hindered carbonyl of the quinone, giving rise to a spiro intermediate **6** and (ii) the latter then undergoes a [3,3] sigmatropic rearrangement to give compound **5**. Although we have no direct evidence for the two-step mechanism suggested here it may be pointed out that the cycloaddition of electron-rich dienes to α -dicarbonyl compounds leading to spirocyclic derivatives is well preceded.²³ It is also noteworthy that such a two-step mechanism has been suggested by Ansell to accommodate the results of the cycloaddition of *o*-chloranil with 2,3-dimethylbutadiene.⁸ The [3,3] sigmatropic rearrangement can be represented as in eqn. (1).



Similarly the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** with hexa-2,4-dienyl acetate in a sealed tube (toluene, 110 °C) gave the benzodioxine **8** in 72% yield (Scheme 2).



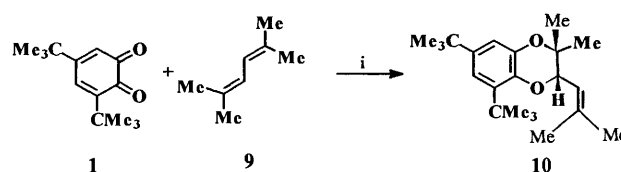
Scheme 2 Reagents and conditions: i, Toluene, sealed tube, 110 °C, 40 h (72%)

Compound **8** shows typical ¹H and ¹³C NMR signals as in the previous case. The ¹H NMR spectrum of compound **8** exhibited a doublet at δ 1.30 ($J = 6.34$ Hz, 3 H) assigned to the methyl protons. The proton adjacent to this methyl group appeared at δ 3.90 as a multiplet. The acetyl group (CH₃CO₂) resonated at δ 2.10. The doublet centred around δ 4.65 ($J = 4.65$ Hz) has been assigned to the CH₂ protons adjacent to the olefinic group. The multiplet at δ 4.15 (1 H) has been assigned to

† In the preliminary communication of this work (V. Nair and S. Kumar, *J. Chem. Soc., Chem. Commun.*, 1994, 1341) we have depicted the benzodioxines as a result of the hetero-Diels–Alder reaction of the 1,4-dioxabutadiene system of the quinone with one of the double bonds of the diene. A close examination of the stereochemistry of the product argues against this mechanistic option. The two-step mechanism suggested here is more likely.

the OCH (in the dioxine ring) adjacent to the olefinic group. The olefinic protons are *trans* (*E*) as indicated by the coupling constant ($J = 12.09$ Hz). The ¹³C signals for the carbons adjacent to oxygen in the benzodioxine ring appeared at δ_C 72.69 and 77.45 in the ¹³C NMR spectrum. The acetyl and methyl carbons appeared at δ_C 20.92 and 17.25 respectively. The CH₂ carbon resonated at δ_C 63.99. The ester carbonyl appeared at δ_C 170.63. The molecular-ion peak at m/z 360 is also in agreement with the proposed structure. The connectivity of protons has been confirmed by 2D COSY experiments. In the COSY spectrum of compound **8** the signal at δ_C 4.10 showed cross-peaks at δ 5.80. The signal at δ 3.88 showed a cross-peak at δ 4.15. The δ 5.83 signal was coupled to the signal at δ 6.05, which has been assigned to the two olefinic protons. The signals at δ 6.05 are further coupled to the signal at δ 4.65. The observed regio- and stereo-chemistry can be explained in terms of an intermediate like that of **6**.

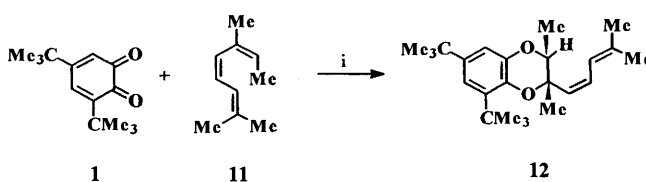
Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** with 2,5-dimethylhexa-2,4-diene **9** gave the benzodioxine adduct **10** as a pale yellow viscous liquid in 84% yield (Scheme 3). This was characterized by spectral analysis.



Scheme 3 Reagents and conditions: i, Neat, sealed tube, 100 °C, 2 h (84%)

The ¹³C signals for carbon atoms adjacent to oxygen in the dioxine ring appeared at δ_C 73.5 and 80.0. The CH proton resonates at δ 3.75 and gives a broad signal. The IR spectrum does not show any carbonyl absorption peaks. The best result for this reaction was obtained when the reagents were heated in a sealed tube without solvent.

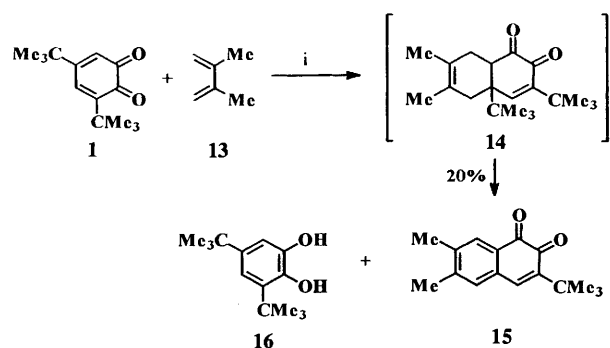
A similar benzodioxine product **12** was isolated from the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** with (*E,E*)-2,6-dimethylocta-2,4,6-triene **11** (alloocimene) (Scheme 4).



Scheme 4 Reagents and conditions: i, CH₂Cl₂, 10 °C, 10 days (75%)

The ¹H NMR spectrum of compound **12** showed a quartet at δ 4.0 (1 H) assigned to the OCH proton in the benzodioxine ring, leading to the conclusion that the addition took place at the 6,7-olefinic bond of alloocimene. The ¹³C signals for carbons adjacent to oxygen in the benzodioxine ring appeared at δ 75.1 and 77.0.

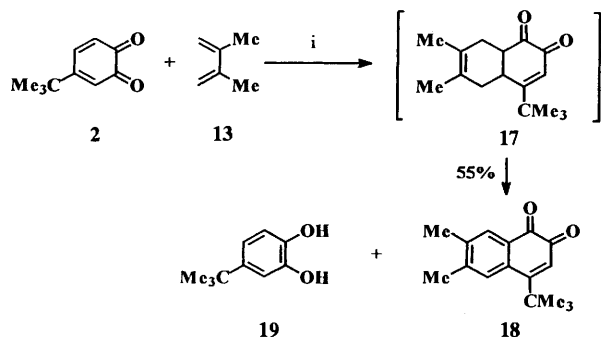
Interestingly, the reaction of 2,3-dimethylbuta-1,3-diene **13** with 3,5-di-*tert*-butyl-*o*-benzoquinone **1** afforded 3-*tert*-butyl-6,7-dimethyl-1,2-naphthoquinone **15** (20%) when the reagents were heated neat in a sealed tube (90 °C); the primary adduct **14** becomes aromatized under the influence of the unchanged quinone present in the reaction mixture. Isolation of 3,5-di-*tert*-butylcatechol **16** from the reaction mixture lends support to the suggested mechanism. The overall reaction can be represented as Scheme 5. The product was characterized by analytical and spectroscopic methods. The *tert*-butyl group in compound **15** appeared as a singlet at δ 1.25 (9 H) and the two methyl groups attached to the aromatic ring appeared as a singlet at δ 2.25



Scheme 5 Reagents and conditions: i, Neat, sealed tube, 90 °C, 8 h

(6 H) in the ^1H NMR spectrum. The proton attached to C-4 of the quinone ring resonated at δ 7.65 as a singlet. The two aromatic protons appeared at δ 6.95 and 7.07. The IR spectrum shows strong carbonyl absorptions at 1670 and 1689 cm^{-1} , suggestive of the presence of quinone carbonyl groups. These carbonyl groups appeared at δ_{C} 206.0 and 208.0 in the ^{13}C NMR spectrum. The molecular-ion peak at m/z 242 is in agreement with the proposed structure.

4-*tert*-Butyl-*o*-benzoquinone **2**, prepared by the oxidation of 4-*tert*-butylcatechol with sodium periodate in aq. CH_2Cl_2 medium, undergoes cycloaddition with 2,3-dimethylbuta-1,3-diene to give the naphthoquinone derivative **18**. Here also it is proposed that the primary adduct **17** undergoes dehydrogenation in the presence of excess of quinone. The final product was isolated in 55% yield (Scheme 6), along with the hydrogenation product 4-*tert*-butylcatechol **19**.



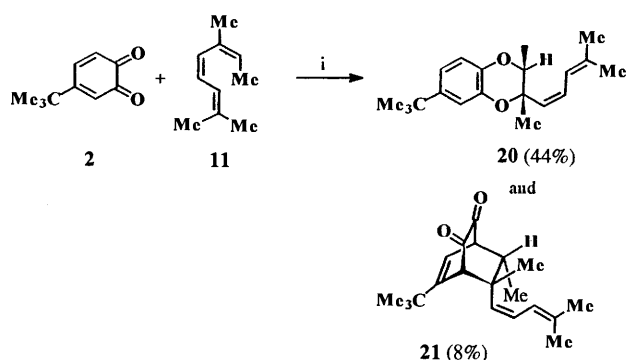
Scheme 6 Reagents and conditions: i, Benzene, reflux, 4 h

The IR spectrum of compound **18** shows the presence of quinone carbonyl at 1656 cm^{-1} . The ^1H NMR spectrum of the product revealed the presence of three proton signals at δ 6.42, 7.7 and 7.95. The signal at δ 6.42 is due to 3-H in the quinone ring. The two peaks at δ_{C} 205.0 and 206.0 in the ^{13}C NMR spectrum have been assigned to the carbonyl carbons. The mass spectrum exhibited a molecular-ion peak at m/z 242.

The reaction of alloocimene **11** and 4-*tert*-butyl-*o*-benzoquinone **2** gave rise to the benzodioxine derivative **20** and the bicyclo[2.2.2]octene dione adduct **21** in 44 and 8% yield; respectively (see Scheme 7).

The product **20** does not show any carbonyl absorption in the IR spectrum. The single proton on the dioxine ring resonated as a quartet at δ 3.96 and it supports the suggested regiochemistry. The signals at δ_{C} 77.0 and 75.0 in the ^{13}C NMR spectrum have been assigned to the two carbon atoms on the dioxine ring. The olefinic and aromatic carbons appeared in the range δ_{C} 114–145. The high-resolution mass spectrum with a molecular-ion peak at m/z 300.2069 is in agreement with the proposed structure.

The adduct **21** is characterized as follows. A strong absorption at 1737 cm^{-1} in the IR spectrum indicates the presence of a saturated carbonyl group. In the ^1H NMR spectrum of **21** the signals at δ 1.0 and 1.2 have been assigned to



Scheme 7 Reagents and conditions: i, Acetonitrile, room temp., 10 days

the bridgehead methyl protons. The two methyl groups on the side chain resonated at δ 1.65 as a singlet. The bridgehead protons displayed a multiplet at δ 3.0. The olefinic protons on the side chain appeared at δ 5.65 (m, 1 H) and 6.5 (m, 2 H). The C=O absorptions in the ^{13}C NMR spectrum appeared at δ_{C} 188.0 and 192.0. High-resolution mass spectroscopy gave the molecular-ion peak at m/z 300.2070.

Conclusions

In conclusion, we have encountered a relatively novel reactivity profile for *o*-benzoquinones with electron-rich acyclic dienes in Diels–Alder reactions. The formation of benzodioxin adducts reported here appears to be a general reaction; the stereochemistry of the adducts can be accounted by a two-step mechanism involving a hetero-Diels–Alder reaction and a subsequent [3,3] sigmatropic rearrangement. The reaction of *o*-benzoquinones with dimethylbutadiene follows an anticipated course leading to substituted naphthoquinones. Yet another reactivity profile is operative in the reaction of 4-*tert*-butyl-*o*-benzoquinone and alloocimene leading to the bicyclo[2.2.2] adduct in addition to the benzodioxine.

Experimental

All mps were determined on a Büchi-530 melting-point apparatus and are uncorrected. Mps are reported only for crystalline compounds. IR spectra were recorded on a Perkin-Elmer Model 882 infrared spectrophotometer. UV spectra were recorded on a Shimadzu UV-2100 spectrometer; ϵ -values are given in units of $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. NMR spectra were recorded on an Hitachi-60, a JEOL EX-90 or a Bruker-300 NMR spectrometer with $[\text{D}_2\text{O}]$ chloroform as solvent. Chemical shifts are given in the δ scale with tetramethylsilane as internal standard. J -Values are given in Hz. Mass spectra were recorded on a Finnigan MAT Model 8430 or a Fisons GC 8000-MD 800 spectrometer. Elemental analyses were carried out using a Perkin-Elmer Elemental Analyser. HPLC was done on a Shimadzu LC-10AS instrument, and MPLC on a Büchi 688 system. Solvents used for the experiments were purified by distillation before use. Column chromatography was done using 100–200 mesh silica gel and appropriate mixtures of light petroleum (distillation range 60–80 °C) and ethyl acetate for elution.

2-Acetoxy-3-(1-acetoxyethenyl)-5,7-bis-(1,1-dimethylethyl)-1,4-benzodioxine **5**

A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** (0.20 g, 0.90 mmol) and 1,4-diacetoxybuta-1,3-diene **4** (0.155 g, 0.90 mmol) in dry toluene (1 cm^3) was deoxygenated, sealed under nitrogen, and heated at 120 °C for 30 h. The solvent was evaporated off under reduced pressure and the product was subjected to chromatography on a silica gel column (5% ethyl acetate–light petroleum) to afford compound **5** as crystals (0.32 g, 90%), mp 113–115 °C; ν_{max} (film)/ cm^{-1} 2967, 2875, 1770, 1679, 1593, 1487, 1422, 1373, 1306, 1219, 1109 and 1004; λ_{max} (MeOH)/nm 212 (ϵ

18 475) and 280 (2200); δ_{H} 7.55 (1 H, d, J 12.53), 6.94 (1 H, d, J 2.35, ArH), 6.84 (1 H, d, J 2.3, ArH), 6.20 (1 H, d, J 3.3), 5.50 (1 H, dd, J 12.53), 4.6 (1 H, dd, J 3.3 and 3.07), 2.12 (3 H, s, 2.12 (3 H, s), 1.36 (9 H, s) and 1.26 (9 H, s); δ_{C} 169.61, 167.5, 144.08, 140.5, 140.0, 138.1, 137.39, 117.03, 112.56, 107.94, 89.32, 70.5, 35.0, 34.46, 31.45, 29.76, 21.08 and 20.58; m/z 391 (76%), 390 (M^+ , 100) and 220 (Found: M^+ , 390.4430. $C_{22}H_{30}O_6$ requires M , 390.4591).

3-(1-Acetoxyprop-1-enyl)-5,7-bis-(1,1-dimethylethyl)-2-methyl-1,4-dioxine 8

A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** (0.20 g, 0.90 mmol) and hexa-2,4-dienyl acetate **7** (0.16 g, 1.14 mmol) in dry toluene (1 cm³) was deoxygenated, sealed under nitrogen, and heated at 110 °C for 40 h. The solvent was removed under reduced pressure and the product was subjected to chromatography on a silica gel column (5% ethyl acetate–light petroleum) to afford compound **8** as crystals (0.234 g, 72%) mp 65–67 °C; v_{max} (film)/cm⁻¹ 2692, 2873, 1749, 1669, 1591, 1484, 1422, 1364, 1309, 1236, 1091, 1031, 972 and 862; δ_{H} 6.85 (2 H, m), 6.05 (1 H, m), 5.83 (1 H, m), 4.65 (2 H, d, J 4.6), 4.15 (1 H, m), 3.88 (1 H, m), 2.10 (3 H, s), 1.35 (9 H, s), 1.30 (3 H, d, J 6.3) and 1.25 (9 H, s); δ_{C} 170.63, 143.28, 142.74, 139.29, 137.60, 128.90, 128.76, 115.69, 111.94, 77.45, 72.69, 63.99, 35.07, 34.37, 31.49, 29.79, 20.92 and 17.25 (Found: M^+ , 360.2287. $C_{22}H_{32}O_4$ requires M , 360.2300).

5,7-Bis-(1,1-dimethylethyl)-2,2-dimethyl-3-(2-methylprop-1-enyl)-1,4-benzodioxine 10

3,5-Di-*tert*-butyl-*o*-benzoquinone **1** (0.20 g, 0.90 mmol) and 2,5-dimethylhexa-2,4-diene **9** (1 cm³, 7.0 mmol) were placed in a tube, which was then sealed under nitrogen. The tube was then heated at 100 °C for 2 h. The excess of diene was removed under reduced pressure and the product was subjected to chromatography on a silica gel column (2% ethyl acetate–light petroleum) to afford compound **10** as a pale yellow oil (0.252 g, 84%); v_{max} (film)/cm⁻¹ 2896, 1589, 1489, 1235, 1029, 976 and 850; δ_{H} 6.60 (2 H, m), 5.75 (1 H, m), 3.75 (1 H, br), 1.45 (6 H, br s), 1.40 (9 H, s), 1.30 (6 H, br s) and 1.20 (9 H, s); δ_{C} 145.0, 143.5, 142.0, 140.5, 137.5, 134.5, 117.5, 115.0, 80.0, 73.5, 35.0, 34.0, 32.1, 32.0, 31.9, 29.75, 29.7 and 29.5; m/z 330 (M^+), 220, 187, 99 and 56 (Found: M^+ , 330.489. $C_{22}H_{34}O_2$ requires M , 330.4909).

5,7-Bis-(1,1-dimethylethyl)-2,3-dimethyl-3-(4-methylpenta-1,3-dienyl)-2,3-dihydro-1,4-benzodioxine 12

3,5-Di-*tert*-butyl-*o*-benzoquinone **1** (0.20 g, 0.907 mmol) and allocimene **11** (0.6 g, 4.3 mmol) were dissolved in CH₂Cl₂ (10 cm³) and kept at 10 °C for 10 days. The solvent was evaporated off and the residue, on column chromatography on silica gel, afforded compound **12** as a pale yellow viscous oil (0.24 g, 75%), v_{max} (film)/cm⁻¹ 2962, 1591, 1468, 1420 and 1037; δ_{H} 6.90 (2 H, br s), 6.5–5.9 (3 H, m), 4.0 (1 H, q, J 6.7), 1.80 (6 H, s), 1.34 (3 H, d, J 6.7), 1.30 (3 H, s), 1.27 (9 H, s) and 1.10 (9 H, s); δ_{C} 142.5, 142.0, 139.5, 139.0, 130.5, 128.0, 126.0, 118.5, 114.0, 77.0, 75.1, 34.5, 34.0, 27.0, 20.5, 20.2, 19.5, 18.5 and 18.0; m/z 356 (M^+), 198, 69 and 54 (Found: C, 80.1; H, 10.0. $C_{24}H_{36}O_2$ requires C, 80.85; H, 10.18%).

3-(1,1-Dimethylethyl)-6,7-dimethyl-1,2-naphthoquinone 15

3,5-Di-*tert*-butyl-*o*-benzoquinone **1** (0.5 g, 2.26 mmol) and 2,3-dimethylbuta-1,3-diene **13** (0.5 g, 6.0 mmol) were placed in a glass tube, which was sealed under vacuum. It was then heated at 90 °C for 8 h. The excess of diene was removed under reduced pressure and the residue, on column chromatography, gave compound **15** as red crystals (0.108 g, 20%), mp 145–147 °C; v_{max} (film)/cm⁻¹ 2965, 2872, 1689, 1670, 1655, 1602, 1451, 1391 and 1292; δ_{H} 7.65 (1 H, s), 7.07 (1 H, s), 6.95 (1 H, s), 2.25 (6 H, s) and 1.25 (9 H, s); δ_{C} 208.0, 206.0, 147.0, 146.0, 139.5, 139.0, 133.5, 131.0, 130.5, 115.5, 35.0, 29.0, 20.0 and 19.5 (Found: M^+ , 242.3003. $C_{16}H_{18}O_2$ requires M , 242.3034).

4-(1,1-Dimethylethyl)-6,7-dimethyl-1,2-naphthoquinone 18

4-*tert*-Butyl-*o*-benzoquinone **2** (0.2 g, 1.21 mmol) and 2,3-dimethylbuta-1,3-diene **13** (0.5 g, 6.08 mmol) were dissolved in benzene (10 cm³) and the solution was refluxed for 4 h under nitrogen. The solvent was evaporated off under reduced pressure and the residue, on silica gel column chromatography [ethyl acetate–light petroleum ether (5:95)], afforded compound **18** as a red solid (0.165 g, 55%), v_{max} (film)/cm⁻¹ 2970, 1656, 1593, 1540, 1393, 1287 and 1187; δ_{H} 7.95 (1 H, s), 7.7 (1 H, s), 6.42 (1 H, s), 2.4 (3 H, s), 2.35 (3 H, s) and 1.5 (9 H, s); δ_{C} 206.0, 205.0, 146.5, 146.0, 140.0, 139.5, 134.0, 131.0, 130.0, 116.0, 35.0, 29.1, 20.0 and 19.5 (Found: C, 81.6; H, 9.1. $C_{16}H_{18}O_2$ requires C, 81.77; H, 9.15%).

Diels–Alder adducts 20 and 21

4-*tert*-Butyl-*o*-benzoquinone **2** (0.207 g, 1.24 mmol) and allocimene **11** (0.5 cm³, 2.9 mmol) were dissolved in acetonitrile (10 cm³) and the solution was stirred at room temperature for 10 days. The solvent was removed, and the residue, on chromatography, afforded adducts **20** (0.164 g, 44%) and **21** (0.022 g, 8%) as viscous oils.

7-(1,1-Dimethylethyl)-2,3-dimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-1,4-benzodioxine **20**. v_{max} (film)/cm⁻¹ 2969, 2877, 1591, 1507, 1381, 1282 and 1075; δ_{H} 6.8 (3 H, m), 5.9 (1 H, m), 5.7 (1 H, m), 5.45 (1 H, m), 3.96 (1 H, q), 1.75 (6 H, br s), 1.3 (6 H, br s) and 1.25 (9 H, s); δ_{C} 145.1, 142.2, 140.2, 137.1, 130.0, 128.0, 124.2, 117.1, 116.1, 114.2, 77.0, 75.0, 34.1, 31.0, 26.0, 23.0, 18.0 and 15.2 (Found: M^+ , 300.2069. $C_{20}H_{28}O_2$ requires M , 300.2089).

5-(1,1-Dimethylethyl)-7,8-dimethyl-8-(4-methylpenta-1,3-dienyl)bicyclo[2.2.2]oct-5-ene-2,3-dione **21**. v_{max} (film)/cm⁻¹ 2966, 2878, 1737, 1676, 1505, 1462, 1373, 1271, 1213, 1089 and 967; δ_{H} 6.5 (2 H, m), 6.0 (1 H, m), 5.65 (1 H, m), 3.0 (3 H, m), 1.65 (6 H, br s), 1.25 (9 H, s), 1.2 (3 H, s) and 1.0 (3 H, d); δ_{C} 192.1, 188.0, 139.2, 133.5, 128.0, 125.0, 124.5, 121.3, 62.0, 54.0, 43.0, 42.1, 35.0, 31.5, 28.0, 27.5, 25.7 and 18.5 (Found: M^+ , 300.2070).

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