Studies in the cyclopropparene series:[1] oxygen-containing 1*H*-cyclopropa[*b*]naphthalenes and their methylidene derivatives

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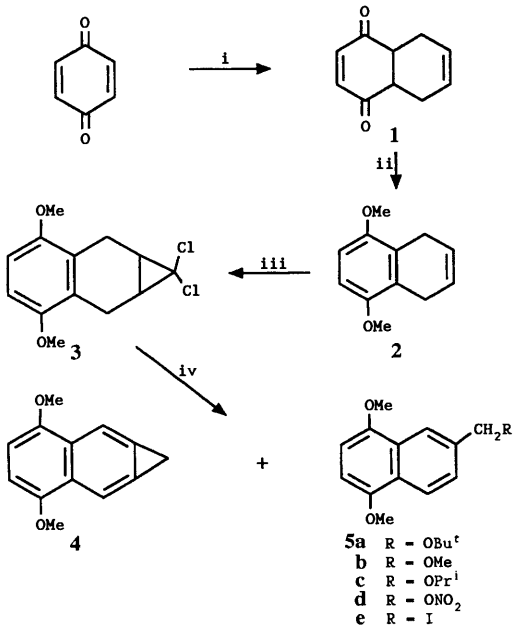
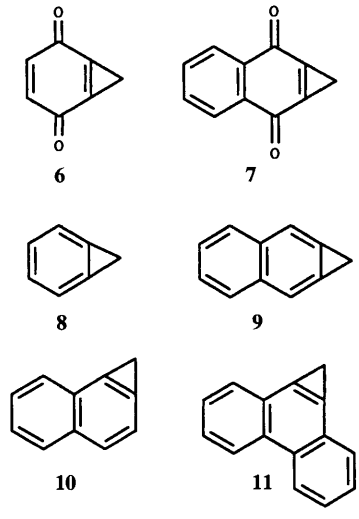
3,6-Dimethoxy-1*H*-cyclopropa[*b*]naphthalene 4 is available from 1,4-benzoquinone in four steps in 27–28% overall yield. The diether 4 provides a range of methylidene derivatives 15a–e by way of the disilyl compound 14, and is efficiently demethylated by cerium(IV) ammonium nitrate to provide 1*H*-cyclopropa[*b*]naphthalene-3,6-dione 16 (85%) whose crystal structure is reported. Quinone 16 is the first stable cyclopropaquinone but it resists conversion into a 1-C exocyclic olefin. The chemistry of the compounds is described, their spectral data are discussed, and the cyclic voltammetry of 16 is provided.

Despite wide interest in the strained cyclopropparenes[2] and their novel methylidene derivatives[3–5] the number of compounds available that carry substituents in the aromatic frame is remarkably few.[6–8] Following our earlier studies involving polar methylidenecyclopropparenes[1] and the observation that certain members of this class are exceptionally fluorescent,[4,9] we became attracted to extended 'push-pull' systems that incorporate electron-donating or electron-withdrawing functionality within the aromatic component of the methylidene derivatives. Coupled with the classical route to the linear cyclopropparene hydrocarbons,[10] the incorporation of oxygen atoms as electron donors within ether functions at C-3 and C-6 of cyclopropa[*b*]naphthalene, as in **4**, was considered entirely plausible by employing the synthetic sequence depicted by Scheme 1. Furthermore, the transformation of these *para*-ether functions into an electron-withdrawing quinone sub-unit as in **16** would provide for complementary, but reversed, electronic influence; such demethylations have adequate literature precedence.[11,12]

Currently there exists no stable cyclopropparene that contains a quinone moiety. While Oda *et al.* provided cyclopropabenzoquinone **6** from flash vacuum pyrolysis methods (and intercepted it in a Diels–Alder cycloaddition with anthracene),[13] Wege and Collis[14] much more recently employed milder desilylation procedures and provided this and cyclopropa[*b*]-naphthalene-2,7-dione **7** as reactive molecules that are captured by furan as [4 + 2] cycloadducts across the cyclopropene π-bond. The location of the quinone moiety adjacent to the sites of ring fusion in **6** and **7** imparts cyclopropene character to the three-membered ring and the compounds are likely to be markedly less stable than analogues such as **16** where the quinone moiety is remote from the small ring. This is directly analogous to the recorded differences between cyclopropa-benzene† **8** and -[*b*]naphthalene **9**, and the angular homologues cyclopropa-[*a*]naphthalene **10** and -[*l*]phenanthrene **11**.[2,15]



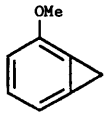
Scheme 1 *Reagents and conditions:* i, buta-1,3-diene, sealed tube, 40 °C; ii, Me_2SO_4, K_2CO_3; iii, :CCl_2; iv, KOBu^t, THF, 0–20 °C



† IUPAC nomenclature names the parent as bicyclo[4.1.0]hepta-1,3,5-triene. For convenience in comparison the term cyclopropabenzene is used throughout.

Results and discussion

Classical[16] Diels–Alder cycloaddition of buta-1,3-diene to freshly sublimed benzoquinone affords enedione **1** (92%) that undergoes methylation and aromatisation to diether **2** (94%) with dimethyl sulfate and potasium carbonate.[17] Dichlorocyclopropanation of **2** parallels the previously reported addition of dibromocarbene[18] and provides the dichlorotetrahydronaphthalene **3** in 72% yield. Upon exposure to *tert*-butoxide in tetrahydrofuran, **3** behaves as expected[2] and undergoes didehydrochlorination to 3,6-dimethoxy-1*H*-cyclopropa[*b*]-naphthalene **4** that is isolated as a colourless crystalline solid in reasonable (44%) yield. To the best of our knowledge, cycloproparene **4** is only the third recorded cycloproparenyl ether; 2-methoxycyclopropabenzene **12** has been studied by



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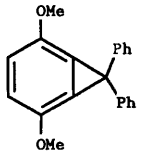
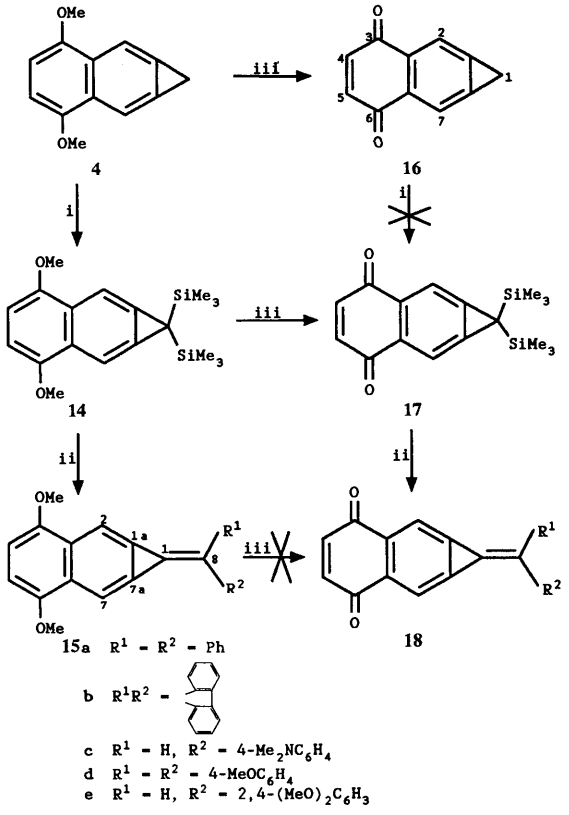


13

Apeloig and Arad[7] and 2,5-dimethoxy-1,1-diphenylcyclopropabenzene **13** was proposed[8] as a reactive intermediate in the photodeazetation of 4,7-dimethoxy-3,3-diphenyl-3*H*-indazole. Compound **4** is somewhat sensitive to air and unless stored under an inert atmosphere it slowly turns pink over a period of weeks. The structure of **4** follows from its mode of formation, is fully supported by its spectroscopic data and is confirmed from ring opening to the 2-naphthalenyl ethers **5a–c** (Scheme 1) under silver(I) catalysis.[19] The ^{1}H NMR spectrum displays four singlets as expected [δ 8.00 (2-H/7-H), 6.72 (4-H/5-H), 3.95 (2 × OMe) and 3.46 (CH_2)] while the ^{13}C NMR spectrum has the carbon atoms adjacent to the three-membered ring (2-C/7-C) typically shielded[2] and at δ 106.8 while 4-C/5-C *ortho* to the ether functions resonate at δ 103.4. The infrared spectrum shows the weak combination band from the three-membered ring and the aromatic double bond at 1760 cm^{-1}.

In addition to cycloproparene **4** the base induced elimination provides the ring opened triether **5a** in 34% yield that is easily separated by conventional chromatographic methods. This is by no means the first report of such a side-product,[19] although the yield is markedly higher perhaps because of the bis-ether functionality. This same compound arises from independent silver(I) catalysed ring cleavage of **4** in *tert*-butyl alcohol. Such electrophilic ring-openings are well known[2] and in the present study the ethers **5a–c** have been obtained from **4** (Scheme 1; see Experimental section). Interestingly, each of these 2-naphthalenylmethyl ethers was accompanied by a second derivative that is proposed as nitrate **5d**, but its appearance is not untoward.[20] The mass spectrum of this compound displays a molecular ion as base peak at *m*/*z* 263 and shows the loss of $NO_2^{\bullet}$ and $NO_3^{\bullet}$ to give major fragments at *m*/*z* 217 and 201, respectively.

Like cyclopropa[*b*]naphthalene **9**,[3,21] compound **4** reacts with butyllithium to provide the corresponding 1-C anion that is intercepted by trimethylsilyl chloride. Whereas the 1-trimethylsilylcyclopropabenzene can be prepared[21,22] from **8**, the monosilyl analogue from **9** eludes isolation and it is the 1,1-bis(trimethylsilyl) derivative that is obtained.[3,21] In order to avoid complications with **4** the procedure for silylation mirrored that for **9**, the didemethoxy parent;[21] the disilyl compound **14** (Scheme 2) was isolated in 71% yield as a stable crystalline solid. The spectroscopic data (Experimental section) are fully in accord with the assigned structure and the cycloproparenyl moiety is confirmed by shielding of 2-C/7-C at δ 102.4. The availability of **14** provides the essential substrate for α-silyl anion generation and Peterson olefination to dimethoxymethylidenecycloproparenes. Indeed, subjection of **14** to the reaction conditions found effective for 1,1-bis-(trimethylsilyl)cyclopropa[*b*]naphthalene[21,23] has provided the exocyclic olefins **15a–e** (Scheme 2) as brightly coloured crystalline compounds in yields ranging from 16 to 71%.



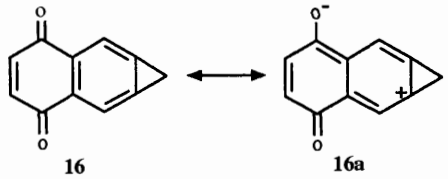
Scheme 2 *Reagents and conditions:* i, BuLi, Me_3SiCl; ii, KOBu^t, R^1R^2CO; iii, $Ce(NH_4)_2(NO_3)_6$ (CAN)

The methylidene diethers **15a–e** are less stable than their non-ether analogues and slowly darken on storage in air—behaviour typical of phenols and many aryl ethers. That the compounds have the assigned structures follows from their spectroscopic data (Experimental section) and by appropriate comparison with the previously reported derivatives with an unsubstituted naphthalenyl moiety.[21,23] Suffice it to say that each of **15a–e** shows a weak infrared stretch in the 1760–1790 cm^{-1} range typical of the family,[2] that the ultraviolet–visible spectra display the expected solvatochromy in their long wavelength absorption bands,[4,21,23–25] and that NMR chemical shifts [assigned with the aid of 2D ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy (COSY) experiments] match expectations especially for 2-C/7-C and the exocyclic olefin 1-C and 8-C.[4,21,23,24] Especially noteworthy here is the observation that 8-C is *more* shielded by *ca.* 2 ppm in **15** than in the non-ether analogues, a feature nicely consistent with expected polarity and electron donation from the 3-C/6-C ether oxygen atoms away from the naphthalenyl moiety.[4,23–26] The cycloproparene 1-C is affected to a much smaller extent but the chemical shifts are actually increased in accord with this expectation. Polarity in the direction of the exocyclic substituent(s) is expected to be maximised in the fluorenylidene **15b** but its limited solubility has precluded polarity measurements. It should be noted that the Peterson olefination route to methylidenecycloproparenes has provided[26] only two derivatives that carry *para*-nitrophenyl electron-withdrawing substituents at 8-C and the procedure has yet to prove effective in the present case. On the other hand, transformation of the aromatic 3,6-dimethoxy function of **15** into a quinone would provide the necessary, and complementary, cycloproparenyl electron sink.

The transformation of *para*-dimethoxy substituted aromatics into 1,4-quinones has been effected with a variety of reagents,

but the present study appeared to demand particularly mild conditions in order to avoid opening the three-membered ring. For the initial study the conversion of **4** into **16** was attempted. Demethylation and oxidation using trimethylsilyl iodide[11] liberated iodine, but no evidence was obtained to support the formation of the sought-after quinone **16**. The complex product mixture provided mass spectral data consistent with the formation of the iodomethylnaphthalene **5e** (*m/z* 328) from opening the three-membered ring of **4**. Upon changing the reagent to cerium(IV) ammonium nitrate (CAN),[12] stirring for thirty minutes at room temperature leads to smooth oxidative demethylation and cyclopropanaphthoquinone **16** (Scheme 2) is isolated as air-sensitive bright yellow needles in 85% yield.

The structure of quinone **16** (ν_{max} 1659 cm^{-1}) was assigned with confidence from the spectroscopic data and is confirmed by X-ray crystal structure analysis (see below). Moreover, treatment of quinone **16** with Ag^{I}–methanol results in ring-opening to known[27] 6-methoxymethylnaphthoquinone. The ^1H NMR spectrum of **16** shows three equal intensity proton singlets at δ 3.36 ($>CH_2$), 6.95 (4-H4/5-H) and 7.90 (2-H/7-H), respectively, while the ^{13}C NMR spectrum provides three protonated and three quaternary carbon resonances as expected. The methylene signal (δ 19.1) is unequivocal, and of the methine signals, that at higher field (δ 112.8) is fully compatible with the shieldings expected[2] for 2-C/7-C of a cyclopropa[*b*]naphthalene; 4-C/5-C of **16** (δ 138.1) match 2-C/3-C of 1,4-naphthoquinone. Heteronuclear correlation spectroscopy (^1H-^{13}C COSY) is fully compatible with these assignments. Of the three quaternary carbon resonances, that at δ 185.2 ppm is due to the quinone carbonyl carbons, but differentiation of the remaining pair (δ 135.4 and 132.5) between C1a/C7a and C2a/C6a is not obvious. Cyclopropabenzene **8** has its bridge carbons at δ 125.4 and cyclopropa[*b*]naphthalene **9** has its two quaternary carbon resonances at δ 123.4 and 136.7;[2,24] reasoned analysis suggests that these resonances are due to C1a/C7a and C2a/C6a, respectively. By use of heteronuclear multiple bond connectivity (HMBC) experiments we now confirm that these assignments for **9** are correct as it is only C1a/C7a (δ 123.4) that correlates with the methylene protons. In like manner an unequivocal assignment of the quaternary resonances of quinone **16** is possible by HMBC. Thus it is the higher field quaternary at δ 132.5 that correlates with both the δ 3.36 (CH_2) and 7.90 (2-H/7-H) proton signals and this must therefore be due to C1a/C7a; the signal at δ 135.4 is due to C2a/C6a as this correlates only with 2-H/7-H. Remarkable here is the dramatic downfield shift of C1a/C7a from its position at δ 123.4 in both diether **4** and parent **9**. We ascribe this 9 ppm deshielding to polar character within the quinone whereby C1a/C7a attains a degree of cationic character as depicted by **16a**. Indeed, this observation further



16 **16a**

encouraged us to pursue the synthesis of various alkylidene-cyclopropanaphthoquinones carrying 8-C electron-donating substituents.

In order to estimate the quinonoid character of **16** electrochemical reduction potentials have been obtained by cyclic voltammetry (CV). These are compared with those of appropriate quinones whose CV data, while known,[28] were also recorded in the present study to provide appropriate checks and to allow for meaningful direct comparison. The values recorded below for benzo-, naphtho- and anthraquinone are within experimental error of those previously

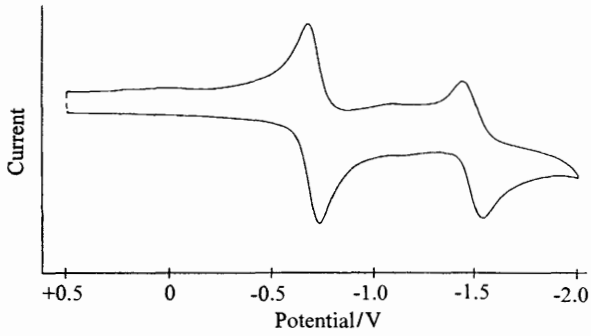


Fig. 1 Cyclic voltammogram of quinone **16** recorded in DMF containing Bu_4NClO_4 (0.1 mol dm^{-3}); Ag/AgCl reference electrode and a scan rate of 100 mV s^{-1}

recorded.[28] As depicted by Fig. 1, the cyclic voltammogram of **16** in DMF (containing tetrabutylammonium perchlorate as supporting electrolyte) shows easy reduction in two reversible one-electron transfers at $E_{\frac{1}{2}}(1)$ at -0.72 and $E_{\frac{1}{2}}(2)$ at -1.49 V, respectively.‡ The first wave produces the radical anion by addition of an electron to the LUMO and the second wave provides the corresponding dianion by subsequent electron addition. By comparison of the first reduction potential of 1,4-benzoquinone [$E_{\frac{1}{2}}(1)$ -0.50, $E_{\frac{1}{2}}(2)$ -1.41 V], 1,4-naphthoquinone [$E_{\frac{1}{2}}(1)$ -0.67, $E_{\frac{1}{2}}(2)$ $-$ 1.50 V] and 9,10-anthraquinone [$E_{\frac{1}{2}}(1)$ -0.94, $E_{\frac{1}{2}}(2)$ -1.66 V],[28] cyclopropaquinone **16** is 0.05 V more difficult to reduce than its naphthoquinone analogue. The difference in the reduction potentials for the first and second waves reflects differences in electrostatic repulsion effects upon going from radical anion to dianion. This value for **16** [$E_{\frac{1}{2}}(1) - E_{\frac{1}{2}}(2) = 0.77$ V] lies midway between those for 1,4-naphthoquinone [$E_{\frac{1}{2}}(1) - E_{\frac{1}{2}}(2) =$ 0.83 V] and 9,10-anthraquinone [$E_{\frac{1}{2}}(1) - E_{\frac{1}{2}}(2) = 0.72$ V] and a hyperconjugative stabilisation of the dianion state by the C–H bonds of the three-membered ring in **16** may be operative.

The formal transformation of **4** into a methylidene-cyclopropanaphthoquinone **18** can occur by any one of three possible routes (Scheme 2). The most obvious approach involves direct demethylation of the methylidenediethers **15** already synthesised. However, all attempts to bring about this transformation, predominantly using **15a** as the model substrate, have been singularly unsuccessful and resulted in surprisingly little chromatographically mobile material (Experimental section); no spectral evidence was gleaned to support the formation of **18a**. An alternative procedure commences with silylation of quinone **16** and subsequent Peterson olefination of the disilylated product **17**. Upon using the conditions found successful[21] for **4**, **8** and **9**, quinone **16** failed to provide the requisite disilyl compound **17**. Even with modifications to the reaction conditions and procedure, all that ensued was significant substrate decomposition without formation of the sought after product. Undeterred by these events we turned our attention to demethylation of the available disilyl compound **14** as the remaining route to **17** (and **18**). While the standard reaction procedure provides a series of orange–red oils, only on one occasion was a sample of compound obtained that was fully compatible with the disilylquinone **17** (23 mg, 25%). We regard this observation as an experimental artefact as the reaction has defied repetition despite many attempts! The product that was formed displayed three proton NMR singlets [δ 0.03 (18 H), 6.88 (2 H) and 7.47 (2 H)] and had a

‡ Corrected values for the reduction potentials of **16** employing ferrocene as internal standard ($E_{\frac{1}{2}}$ 0.089 V) are **16**: $E_{\frac{1}{2}}(1)$ -0.983 and $E_{\frac{1}{2}}(2)$ -1.732 V, respectively. We thank Professor K. Komatsu (Kyoto University) for these measurements and for checking our data.

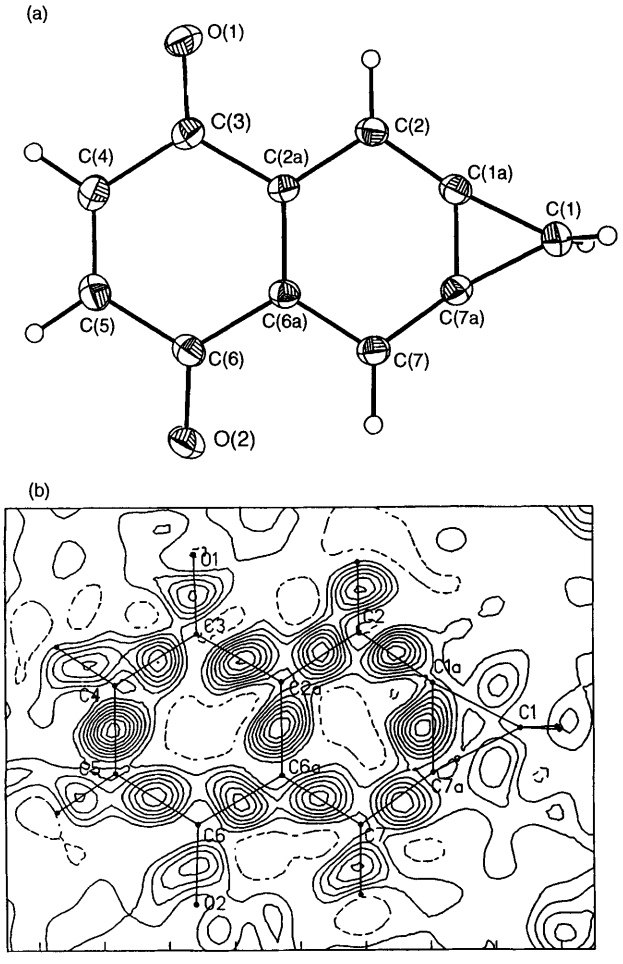


Fig. 2 X-Ray structure of quinone **16** (*a*) with systematic crystallographic labelling of the atoms, and (*b*) as an X–X difference electron density map (contours every 0.05 e Å^{-3})

weak (4%) molecular ion (*m*/*z* 314) in the mass spectrum fully in accord with formation of the desired quinone. Unfortunately the compound was not present in sufficient quantity for assessment of its potential as a progenitor of **18**; methylidenecyclopropaquinones thus remain a challenge for synthesis.

X-Ray crystal structure of 1 *H*-cyclopropa[*b*]naphthalene-3,6-dione 16

As quinone **16** is the only stable cyclopropaquinone currently available an investigation of the structural features of the compound has been undertaken. As depicted in Fig. 2(*a*) compound **16** is confirmed as the requisite cyclopropaquinone and relevant bond lengths and angles are listed in Table 1. The crystal structure of **16** consists of well separated molecules, there are no significant intermolecular H · · · H contacts and the molecule adopts an almost planar arrangement with the three-membered ring displaced from the plane by 2.2° as is typical for the cycloproparenes.[2,29] The impact of conversion of the cyclopropareneinto its corresponding quinone is shown in the various bond lengths recorded. Thus the quinone ring bonds C(4)–C(5) and C(2a)–C(6a) of **16** are *shorter* than those of **9** by 0.08 and 0.03 Å, respectively, while C(3)–C(4)/C(5)–C(6), and C(2a)–C(3)/C(6)–C(6a) are elongated by 0.10 and 0.07 Å, respectively. This distortion is transferred to the cyclopropa-fused ring as bonds C(2)–C(2a)/C(6a)–C(7) are *shortened* by 0.03 Å while strain release is evidenced by a *lengthening* of bonds C(1a)–C(2)/C(7)–C(7a) by *ca.* 0.15 Å in comparison with **9**. The lengthening of these last two bonds in **16** results in a 0.02 Å *reduction* in the length of the bridge bond [C(1a)–C(7a)] to 1.353 Å. In comparison to 1,4-naphthoquinone,[30] the distances

Table 1 Selected bond lengths and angles for cyclopropaquinone **16**

Bond lengths/Å		Interbond angles (°)	
O(1)–C(3)	1.227(2)	C(1A)–C(1)–C(7A)	53.5(1)
O(2)–C(6)	1.223(2)	C(1)–C(1A)–C(7A)	63.2(1)
C(1)–(1A)	1.506(2)	C(1)–C(7A)–C(1A)	63.4(1)
C(1)–C(7A)	1.503(2)	C(1)–C(1A)–C(2)	171.7(1)
C(1A)–C(7A)	1.353(2)	C(2)–C(1A)–C(7A)	124.8(1)
C(1A)–C(2)	1.370(2)	C(1A)–C(2)–C(2A)	112.9(1)
C(2)–C(2A)	1.415(2)	C(2)–C(2A)–C(6A)	122.1(1)
C(2A)–C(3)	1.487(2)	C(3)–C(2A)–C(6A)	119.7(1)
C(2A)–C(6A)	1.416(2)	C(2A)–C(3)–C(4)	118.4(1)
C(3)–C(4)	1.478(2)	C(3)–C(4)–C(5)	121.8(1)
C(4)–C(5)	1.334(2)	C(4)–C(5)–C(6)	121.8(1)
C(5)–C(6)	1.479(2)	C(5)–C(6)–C(6A)	118.4(1)
C(6)–C(6A)	1.487(2)	C(2A)–C(6A)–C(6)	119.7(1)
C(6A)–C(7)	1.412(2)	C(2A)–C(6A)–C(7)	122.3(1)
C(7)–C(7A)	1.369(2)	C(6A)–C(7)–C(7A)	112.8(1)
		C(1A)–C(7A)–C(7)	125.1(1)
		C(1)–C(7A)–C(7)	171.5(1)

in the cyclopropa-fused ring of **9** are shorter by *ca.* 0.2 Å. Given these latter data, the differences match expectations for the transformation of hydrocarbon **9** to quinone **16**. A discussion of the structures of various cycloproparenes has appeared[29] and in this context it is worthy of mention that the sum of the bond lengths in the naphthalenyl moiety of **16** (15.6 Å) is very similar to that of cyclopropanaphthalene **9** itself (15.4 Å). The lengths of the three-membered ring σ-bonds [C(1)–C(1a)/(7a)] are unaffected by the chemical transformation and are the same as in **9**. The interbond angles (Table 1) recorded for **16** are typical of the cycloproparenes and complement those found for **9**. Moreover, the X–X electron density distribution [Fig. 2(*b*)] again demonstrates the effect of bent bonds in the cycloproparenes[29] by an exocyclic shift of the density maxima in the three-membered ring of **16** and the adjacent [C(1a)–C(2) and C(7)–C(7a)] aromatic bonds.

Experimental

Melting points were determined using a Reichert Thermovar hot-stage apparatus and are uncorrected. Microanalyses were performed by the microanalytical facility of the University of Otago, Dunedin, New Zealand. Low-resolution mass spectra were recorded at 70 eV on a Hewlett-Packard 5995, and accurate mass data were from a Kratos MS80 RFA instrument. IR spectra were recorded for KBr disks on a BIORAD FTS-7, UV–VIS spectra on a Hewlett-Packard 8452A Diode Array Spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Associates FT80A or a Bruker AC 300E instrument at 79.56 and 20.00, and 300 and 75 MHz, respectively, in [^{2}H]chloroform solutions with tetramethylsilane as internal standard; *J* values are given in Hz.

Cyclic voltammograms were obtained from a Princeton Applied Research Model 362 scanning potentiostat with measurements at 20 °C in dry degassed dimethylformamide under a nitrogen atmosphere. Tetrabutylammonium perchlorate (1.0 mol dm^{-3}) was employed as supporting electrolyte; the working electrode was Pt, the auxiliary electrode W and the reference electrode Ag/AgCl. Substrates were present at *ca.* 10 mmol dm^{-3}.

Merck silica gel grade 60, 230–400 mesh, 60 Å was used for flash column chromatography. DC-Alufolien Kieselgel 60 F254 (layer thickness: 0.2 mm) was used for all TLC analyses. Radial chromatograms employed Merck silica gel 60 PF254 with plates coated to a thickness of 4 mm. Solvents were purified using procedures in Perrin, Armarego and Perrin.[31] Tetrahydrofuran (THF) was distilled from potassium–benzophenone immediately before use. Potassium *tert*-butoxide was sublimed before use using a Büchi GKR-51 ball oven in sublimation mode.

4a,5,8,8a-Tetrahydronaphtho-1,4-quinone 1

The tetrahydronaphthoquinone **1** was prepared by a modification of the early literature method.[16] Thus to a mixture of freshly sublimed *p*-benzoquinone (15 g, 0.14 mol) and benzene (60 cm^3) in a precalibrated Carius tube, cooled in liquid air, was added by vapour transfer through a long syringe needle buta-1,3-diene (15 g, 24.2 cm^3, 0.28 mol). The tube was sealed, slowly warmed to 40 °C and stirred at this temperature for 4–5 days by which time the solution was a pale yellow–green. After opening the Carius tube at low (−180 °C) temperature, very cautious and slow warming to ambient is essential before the excess diene and solvent can be removed under reduced pressure. The residual pale yellow solid thus obtained was recrystallised (light petroleum) to give **1** as colourless needles (20.9 g, 92%), mp 55–56 °C (lit.,[16] 58 °C); δ_H 1.9–2.6 (m, 2 × CH_2), 3.1–3.3 (m, 4a/8a-H), 5.70 (s, 6/7-H) and 6.67 (s, 2/3-H); δ_C 24.2 (C-5/8), 46.3 (C-4a/8a), 124.4 (C-6/7), 139.3 (C-2/3) and 182.5 (C-1/4); ν_{max}/cm^{-1} 1677; *m/z* 162 (33, M), 134 (50), 133 (39), 116 (22.5), 115 (35), 91 (37), 79 (81), 77 (80) and 54 (100%).

5,8-Dimethoxy-1,4-dihydronaphthalene 2

The dimethoxydihydronaphthalene **2** was obtained by reaction of enedione **1** (13 g, 0.08 mol) with dimethyl sulfate (25.3 g, 19 cm^3, 0.2 mol) in the presence of base[17] and used without further purification (14.4 g, 94%); mp 48.5–49.5 °C (lit.,[17] 50–51 °C); δ_H 3.26 (broad s, 4 H), 3.76 (s, 2 × OMe), 5.86 (broad s, 2/3-H) and 6.61 (s, 6/7-H); δ_C 24.4 (C-1/4), 55.7 (2 × OMe), 107.2 (C-6/7), 123.7 (C-2/3), 124.6 (C-4a/8a) and 151.2 (5) (C-5/8).

1,1-Dichloro-3,6-dimethoxy-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene 3

Method A. To a chilled (0 °C) solution of dimethoxydihydronaphthalene **2** (13 g, 0.068 mol) and benzyltriethylammonium chloride (0.92 g, 0.004 mol) in chloroform (90 cm^3) was added over 1 h sodium hydroxide (50% aqueous, 90 cm^3). The resultant two-phase system was stirred for 48 h at 15 °C after which time the phases were separated. The aqueous solution was extracted with chloroform (2 × 50 cm^3) and the combined organic phases were washed (water, 3 × 80 cm^3), dried (Na_2SO_4), filtered and the filtrate concentrated under reduced pressure to a brown viscous oil. The oil was successively heated under reflux with portions of light petroleum (3 × 20 cm^3), the hot solvent decanted and the combined solvent portions reduced to *ca.* 40 cm^3 after which the solution was cooled to −10 °C whereupon 1,1-*dichloro*-3,6-*dimethoxy*-1*a*,2,7,7*a*-*tetrahydro*-1H-*cyclopropa*[b]*naphthalene* **3** appeared as white crystals (13.3 g, 72%), mp 98–98.5 °C (Found: C, 57.3; H, 5.1; Cl, 26.4. $C_{13}H_{14}Cl_2O_2$ requires C, 57.3 (5); H, 5.1 (5); Cl, 26.1%); δ_H 2.01 (d, *J* 6.1, 1a/7a-H); 2.78 (d, J_{AB} 18.1, 2 H), 3.12 (dd, J_{AB} 18.1, J_{AC} 5.5, 2 H), 3.76 (s, 2 × OMe) and 6.58 (s, 4/5-H); δ_C 18.1 (5) (C-2/7), 25.1 (C-1a/7a), 55.6 (2 × OMe), 65.7 (C-1), 106.5 (C-4/5), 122.9 (C-2a/6a) and 150.9 (C-3/6); *m/z* 276 (12), 274 (64), 272 (96, M), 259 (12), 257 (19, M − Me), 243 (8), 241 (13, M − OMe), 239 (15), 237 (41, M − Cl), 224 (6), 222 (22, M − Cl − Me), 223 (12), 221 (22, M − Me − HCl), 209 (9), 207 (24, M − Cl − MeO), 202 (100, M − Cl − Cl), 201 (43, M − Cl − HCl) and 115 (99).

Method B. To a stirred suspension of **2** (13 g, 0.068 mol) and NaOMe (11.0 g, 0.20 mol) in benzene–light petroleum (1 : 1, 100 cm^3) at 0 °C was added dropwise with stirring over 1 h ethyl trichloroacetate (26.8 g, 19.5 cm^3, 0.14 mol). The cold bath was removed, the mixture stirred for 16 h and water (100 cm^3) added. The organic phase was separated and the aqueous phase extracted with benzene (50 cm^3). The combined organic extracts were washed (water, 3 × 75 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to a brown solid (17.2 g). Recrystallisation (light petroleum) afforded **3** (14.0 g, 76%) as colourless crystals, mp 98 °C, identical to the sample from above.

3,6-Dimethoxy-1*H*-cyclopropa[*b*]naphthalene 4

To potassium *tert*-butoxide (27 g, 0.23 mol) in dry tetrahydrofuran (100 cm^3) at 0 °C was added a solution of the tetrahydrocyclopropanaphthalene **3** (4.0 g, 0.015 mol) in the same solvent (70 cm^3) with stirring over 1 h. The temperature was raised to room temperature and the stirring continued for 48 h whereupon the solvent was removed under reduced pressure and the residual orange solid partitioned with light petroleum–water (1 : 1, 400 cm^3). The phases were separated, the aqueous phase extracted with light petroleum (200 cm^3) and the combined organic extracts washed, (water, 3 × 100 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to a dirty yellow solid (3.44 g) that consisted of two components (TLC). Radial chromatography (dichloromethane–light petroleum, 1 : 4 elution) afforded two fractions A and B.

Fraction A yielded 3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **4** (1.5 g, 51%) as the most mobile fraction. Recrystallisation (light petroleum) gave colourless needles (1.3 g, 44%), mp 130–131.5 °C [Found: C, 78.0; H, 5.8 (5); (HRMS): (M^+) 200.0834. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%; *M*, 200.0837]; δ_H 3.46 (s, CH_2), 3.95 (s, 2 × OMe), 6.72 (s, 4/5-H) and 8.01 (s, 2/7-H); δ_C 18.1 (C-1), 55.9 (2 × OMe), 103.4 (C-4/5), 106.8 C-2/7), 123.4 (C-1a/7a), 128.9 (C-2a/6a) and 150.4 (C-3/6); ν_{max}/cm^{-1} 1760 and 1668; *m/z* 200 (97, M), 185 (100, M − Me), 157 (16, M − MeCO), 127 (28, $C_{10}H_7$) and 114 (22).

The less mobile fraction B afforded colourless needles of 1,4-*dimethoxy*-6-(tert-*butoxymethyl*)*naphthalene* **5a** (1.41 g, 34%), mp 70–71 °C (Found: C, 74.5; H, 8.1. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.0%); δ_H 1.32 (s, $OCMe_3$), 3.93 (s, 2 × OMe), 4.60 (s, OCH_2Ar), 6.66 (s, 2/3-H), 7.46 (d, J_{ortho} 7.5, 7-H), 8.11 (broad s, 5-H) and 8.16 (d, J_{ortho} 7.5, 8-H); δ_C 27.9 ($OCMe_3$), 55.8 (2 × OMe), 64.6 (OCH_2Ar), 73.5 (5) ($OCMe_3$), 103.2/103.6 (C-2/3), 120.0/122.0/125.8 (aromatic CH), 126.5, (C-4a/8a), 137.8 (C-6) and 149.8 (C-1/4); *m/z* 274 (100, M), 259 (24, M − Me), 203 (17, M − Me − C_4H_8), 201 (39, M − OBu^t) and 189 (27%, M − CH_2OBu^t).

Alcoholyses of 3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 4

A solution of cycloproparene **4** (66 mg, 0.33 mmol) in carbon tetrachloride (6 cm^3) was added, with stirring, to a solution of silver nitrate (22 mg, 0.13 mmol) in the requisite alcohol (60 cm^3). After 30 min of stirring the volatiles were removed under reduced pressure and the residue that remained was extracted with ether (80 cm^3). The organic solution was washed (water, 3 × 40 cm^3), dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The residue was shown (TLC) to contain two components A and B that were separated by radial chromatography (dichloromethane–light petroleum, 1 : 1 elution).

***(a)* From reaction in *tert*-butyl alcohol.** Component A, a colourless oil, is proposed as 1,4-dimethoxy-6-(nitratomethyl)-naphthalene **5d** (22 mg, 25%)—see (*c*) below.

Component B is identified as the *tert*-butoxy ether **5a** (47 mg, 51%) identical to the sample obtained as side-product in the preparation of **4**.

***(b)* From reaction in methanol.** Component A, a colourless oil is proposed as 1,4-dimethoxy-6-(nitratomethyl)naphthalene **5d** (6 mg, 7%)—see (*c*) below.

Component B, a pale yellow oil, is identified as 1,4-*dimethoxy*-6-(*methoxymethyl*)*naphthalene* **5b** (65 mg, 83%) [Found (HRMS): (M^+) 232.1097. $C_{14}H_{16}O_3$ requires *M*, 232.1099]; δ_H 3.39 (s, $ArCH_2OMe$), 3.94 (s, 2 × OMe), 4.62 (s, $ArCH_2O$), 6.68 (s, 2/3-H), 7.47 (dd, J_{ortho} 8.5, J_{meta} 1.2, 7-H), 8.13 (broad s, 5-H) and 8.19 (d, J_{ortho} 8.5, 8-H); δ_C 55.8 (2 × $ArOMe$), 58.0 ($ArCH_2OMe$), 75.0 (5) ($ArCH_2O$), 103.5/103.8 (C-2/3), 120.7/122.3/125.7 (aromatic CH) and 149.8 (5) (C-1/4); *m/z* 233 (15), 232 (100, M) and 217 (83, M − Me).

***(c)* From reaction in propan-2-ol.** Component A, a colourless oil, is proposed as 1,4-dimethoxy-6-(nitratomethyl)naphthalene

5d (38 mg, 44%); δ_H 3.95 (s, 2 × ArO*Me*), 5.58 (s, ArCH_2ONO_2), 6.73 (s, 2/3-H), 7.47 (broad d, J_{ortho} 8.5, 7-H), 8.22 (d, J_{ortho} *ca.* 8.5, 8-H) and 8.26 (s, 5-H); *m/z* 264 (15), 263 (100, M), 217 (56, M − NO_2), 202 (42, M − $MeNO_2$), 201 (80, M − ONO_2), 189 (67), 187 (36) and 174 (31).

Component B, a dark brown oil, is proposed as 1,4-dimethoxy-6-isopropoxymethylnaphthalene **5c** (37 mg, 43%); δ_H 1.22 (d, *J* 6.0, (Me_2CH), 3.70 (septet, *J* 6.0, C*H*Me_2), 3.94 (s, 2 × ArO*Me*), 4.67 (s, ArCH_2OPr^i), 6.67 (s, 2/3-H), 7.51 (broad d, J_{ortho} 8.5, 7-H), 8.12 (s, 5-H) and 8.17 (d, J_{ortho} 8.5, 8-H); δ_C 22.2, (Me_2CH), 55.8 (2 × ArO*Me*), 70.4 (ArCH_2O), 70.9 (O*C*HMe_2), 103.3/103.7 (C-2/3), 120.3/122.1/125.8 (aromatic CH), 125.9 (C-6), 136.9 (C-4a/8a) and 149.7 (C-1/4); *m/z* 261 (17), 260 (93, M), 245 (25, M − Me), 203 (21), 202 (71, M − Me_2CO), 201 (46, M − OPr^i), 187 (100, M − CH_2OPr^i), 171 (86), 159 (23), 144 (19), 143 (49), 115 (69) and 100 (49).

1,1-Bis(trimethylsilyl)-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 14

The title compound was prepared by applying the original silylation method[21] to **4** (420 mg, 2.1 mmol). Recrystallisation of the crude orange solid product (light petroleum) afforded 1,1-*bis*(*trimethylsilyl*)-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **14** (512 mg, 71%) as colourless platelets, mp 144–145 °C (Found: C, 66.3; H, 7.9. $C_{19}H_{28}O_2Si_2$ requires C, 66.3; H, 8.1%); δ_H 0.01 (s, 2 × $SiMe_3$), 3.95 (s, 2 × OMe), 6.68 (s, 4/5-H) and 7.51 (s, 2/7-H); δ_C −1.24 (2 × $SiMe_3$), 29.74 (C-1), 59.92 (2 × OMe), 102.41 (C-2/7), 103.73 (C-4/5) and 127.79 (C-2a/6a), 131.41 (C-1a/7a) and 150.24 (C-3/6); *m/z* 344 (36, M), 329 (83, M − Me) and 73 (100, $SiMe_3$).

The 1-methylidene-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalenes 15a–e

The exocyclic olefins **15a–e** were prepared from the disilyl compound **14** according to the original literature procedure[21] on the scale and with the yields that are recorded below.

***(a)* With benzophenone.** The disilyl compound **14** (300 mg, 0.88 mmol) and benzophenone (160 mg, 0.88 mmol) gave 1-*diphenylmethylidene*-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **15a** (180–186 mg, 55–58%) as yellow needles (light petroleum), mp 188–189 °C [Found: C, 83.9; H, 5.6; (HRMS): (M^+) 364.1476. $C_{26}H_{20}O_2 \cdot \frac{1}{2}H_2O$ requires C, 83.6; H, 5.7; *M*, 364.1463]; δ_H 3.96 (s, 2 × OMe), 6.73 (s, 4/5-H), 7.31–7.36 (m, 2 H), 7.42–7.47 (m, 4 H), 7.71 (d, *J* 7.3, 2 H) and 7.98 (s, 2/7-H); δ_C 55.96 (2 × $SiMe_3$), 102.16 (C-2/7), 104.54 (C-4/5), 112.40 (C-1), 118.67 (C-8), 127.15 (C-12/12′), 127.42 (C-2a/6a), 128.11 (C-10/14/10′/14′), 128.41 (C-11/13/11′/13′), 131.26 (C-1a/7a), 139.60 (C-9/9′) and 150.63 (C-3/6); λ_{max}(cyclohexane)/nm 273.5 (log ε 4.00), 317.5 (4.31), 408 (4.43) and 433.5 (4.44); λ_{max}(acetonitrile)/nm 274 (log ε 3.98), 319 (4.21), 407 (4.32) and 430.5 (4.32); ν_{max}/cm^{-1} 2923, 1775, 1612, 1463, 1393, 1261, 1224, 1105, 804, 773, 722 and 697; *m/z* 365 (30, M + 1), 364 (100, M), 349 (29, M − Me) and 334 (80, M − 2Me).

***(b)* With fluorenone.** The disilyl compound **14** (100 mg, 0.29 mmol) and fluorenone (54 mg, 0.30 mmol) gave 1-*fluorenylidene*-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **15b** as a sparingly soluble yellow solid (74 mg, 71%), mp 280 °C (sublim.) [Found: C, 83.3; H, 4.9; (HRMS): (M^+) 362.1317. $C_{26}H_{18}O_2 \cdot \frac{1}{2}H_2O$ requires C, 83.5 H, 5.1; *M*, 362.1307]; δ_H 4.03 (s, 2 × OMe), 6.82 (s, 4/5-H), 7.40 (m, 4 H), 7.83 (d, *J* 6.5, 2 H), 8.17 (d, *J* 6.5, 2 H) and 8.33 (s, 2/7-H); λ_{max}(cyclohexane)/nm 277 (log ε 4.13), 322 (3.82), 432.5 (4.21) and 467 (4.40); λ_{max}(acetonitrile)/nm 275.5 (log ε 4.25), 431.5 (4.05) and 464.5 (4.17); ν_{max}/cm^{-1} 2951, 1788, 1771, 1615, 1521, 1465, 1442, 1331, 1263, 1205, 1177, 1143, 1101, 851, 809, 772 and 728; *m/z* 363 (29, M + 1), 362 (100, M), 347 (10, M − Me) and 332 (61, M − 2Me).

***(c)* With 4-(dimethylamino)benzaldehyde.** The disilyl compound **14** (100 mg, 0.29 mmol) and 4-(dimethylamino)benzaldehyde (45 mg, 0.30 mmol) gave 1-[(4-*dimethylaminophenyl*)-*methylidene*]-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **15c** as orange crystals (light petroleum) (61 mg, 63%), mp 164–165 °C [Found: C, 77.5; H, 6.2; (HRMS): (M^+) 331.1574. $C_{22}H_{21}NO_2 \cdot \frac{1}{2}H_2O$ requires C, 77.2; H, 6.5; *M*, 331.1572]; δ_H 2.92 (s, NMe_2), 3.87 (s, OMe), 3.89 (s, OMe), 6.41 (s, 8-H), 6.63 (s, 4/5-H), 6.71 (d, *J* 8.8, 11/13-H), 7.59 (d, *J* 8.8, 10/14-H), 7.73 (d, J_{para} 1.75, 7-H) and 7.89 (d, J_{para} 1.75, 2-H); δ_C 40.35 (NMe_2), 55.82 (2 × OMe), 101.07/101.09 (C-2/7), 104.09/104.24 (C-4/5), 106.83 (C-8), 108.34 (C-1), 112.56 (C-11/13), 126.04/126.51 (C-1a/7a), 127.41 (C-10/14), 128.28 (C-9), 130.16/130.94 (C-2a/6a), 149.44 (C-12) and 150.40/150.49 (C-3/6); λ_{max}(cyclohexane)/nm 289 (log ε 4.38), 425.5 (4.48) and 457.5 (4.59); λ_{max}(acetonitrile)/nm 293 (log ε 4.77), 426.5 (4.50) and 456.5 (4.95); ν_{max}/cm^{-1} 1776, 1609, 1527, 1503, 1460, 1436, 1365, 1321, 1258, 1214, 1177, 1182, 1169, 1106, 854, 821, 787 and 721; *m/z* 332 (25, M + 1), 331 (100, M), 316 (14, M − Me) and 301 (88, M − 2Me).

***(d)* With 4,4′-dimethoxybenzophenone.** The disilyl compound **14** (100 mg, 0.29 mmol) and 4,4′-dimethoxybenzophenone (70 mg, 0.29 mmol) gave 1-[*di*(4-*methoxyphenyl*)*methylidene*]-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **15d** as yellow crystals (dichloromethane–light petroleum, 1:3) (20 mg, 16%), mp 157–158 °C [Found (HRMS): (M^+) 424.1685. $C_{28}H_{24}O_4$ requires *M*, 424.167 45]; δ_H 3.88 (s, 12/12′-OMe), 3.97 (s, 3/6-OMe), 6.74 (s, 4/5-H), 7.00 (d, *J* 8.8, 11/13/11′/13′-H), 7.70 (d, *J* 8.8, 10/14/10′/14′-H) and 7.88 (s, 2/7-H); δ_C § 55.39 (C-12/12′-OMe), 56.02 (C-3/6-OMe), 101.97 (C-2/7), 104.50 (C-4/5), 113.90 (C-11/11′/13/13′), 127.83 (C-1a/7a), 129.36 (C-10/10′/14/14′), 130.92 (C-2a/6a), 132.32 (C-9/9′), 150.64 (C-3/6) and 159.0 (C-12/12′); λ_{max}(cyclohexane)/nm 274 (log ε 4.13), 319.5 (3.99), 417 (4.14) and 445.5 (4.23); λ_{max}(acetonitrile)/nm 279.5 (log ε 4.35), 320.5 (4.30) 416.5 (4.43) and 444 (4.50); ν_{max}/cm^{-1} 2962, 2925, 1770 (v weak), 1606, 1510, 1464, 1321, 1249, 1223, 1182, 1104, 1027 and 797; *m/z* 425 (32, M + 1), 424 (100, M), 409 (20, M − Me), 394 (49, M − 2Me) and 379 (30, M − 3Me).

***(e)* With 2,4-dimethoxybenzaldehyde.** The disilyl compound **14** (150 mg, 0.44 mmol) and 2,4-dimethoxybenzaldehyde (75 mg, 0.45 mmol) gave 1-[2,4-*dimethoxyphenyl*)*methylidene*]-3,6-*dimethoxy*-1H-*cyclopropa*[b]*naphthalene* **15e** as yellow crystals (dichloromethane–light petroleum, 1:9) (93 mg, 61%), mp 167–168 °C [Found: C, 74.4; H, 5.8; (HRMS): (M^+) 348.1358. $C_{22}H_{20}O_4$ requires C, 73.9; H, 5.9%; *M*, 348.136 15]; δ_H 3.86/3.89 (both s, 10/12-OMe), 3.96/3.97 (both s, 3/6-OMe), 6.50 (d, J_{meta} 2.4, 11-H), 6.64 (dd, J_{ortho} 8.6, J_{meta} 2.4, 13-H), 6.73 (s, 4/5-H), 6.87 (s, 8-H), 7.87 (d, J_{para} 1.8, 7-H), 8.00 (d, J_{para} 1.8, 2-H) and 8.05 (d, J_{ortho} 8.6, 14-H); δ_C 55.47/55.73 (C-10/12-OMe), 55.98 (C-3/6-OMe), 98.53 (C-11), 100.33 (C-8), 101.90/101.93 (C-2/7), 104.27 (C-7), 104.41 (C-4/5), 105.50 (C-13), 110.17 (C-1), 120.22 (C-9), 126.43 (C-14), 126.41/128.10 (C-1a/7a), 130.52/131.27 (C-2a/6a), 150.61/150.68 (C-3/6), 157.35 (C-12) and 160.00 (C-10); λ_{max}(cyclohexane)/nm 306 (log ε 3.97), 320 (3.97), 408.5 (4.36) and 438.5 (4.45); λ_{max}(acetonitrile)/nm 306 (log ε 4.24), 321.5 (4.23), 408 (4.57) and 437 (4.63); ν_{max}/cm^{-1} 2962, 1775 (v weak), 1613, 1604, 1581, 1494, 1464, 1435, 1372, 1321, 1295, 1270, 1259, 1210, 1195, 1103, 1031, 857, 820, 793 and 722; *m/z* 349 (23, M + 1), 348 (100, M), 333 (22, M − Me), 318 (51, M − 2Me) and 317 (58, M − OMe).

1*H*-Cyclopropa[*b*]naphthalene-3,6-dione 16

To a stirred solution of dimethoxycyclopropanaphthalene **4** (520 mg, 0.26 mmol) in acetonitrile–dichloromethane (3:2, 25 cm^3) was added dropwise cerium(IV) ammonium nitrate (4.3 g, 0.78 mmol) in water (20 cm^3). The resultant orange

§ Solubility and sample size precluded observation of the olefinic quaternary carbon atoms 1-C and 8-C.

solution was stirred for a further 30 min after which time it was extracted with dichloromethane (2 × 30 cm^3). The combined organic extracts were washed (water, 3 × 30 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure to a brown solid (665 mg) shown to contain two components (R_F 0.35 and 0.0) by TLC (dichloromethane–light petroleum, 1:2).

Column chromatography (silica gel; 1:1 dichloromethane–light petroleum elution) provided, as the mobile fraction, a bright yellow solid which gave 1H-*cyclopropa*[b]*naphthalene*-3,6-*dione* **16** (375 mg, 85%) as fine yellow needles (dichloromethane–light petroleum, 1:2, −40 °C), mp 130–132 °C (dec.) (Found: C, 77.4; H, 3.5. $C_{11}H_6O_2$ requires C, 77.6; H, 3.6%); δ_H 3.36 (s, CH_2), 6.95 (s, 4/5-H) and 7.90 (s, 2/7-H); δ_C 19.1 (C-1), 112.8 (C-2/7), 132.5 (C-1a/7a), 135.4 (C-2a/6a), 138.1 (C-4/5) and 185.2 (C-3/6); λ_{max}(cyclohexane)/nm 268 (log ε 3.23) and 333 (3.36); λ_{max}(acetonitrile)/nm 287.5 (log ε 3.61) and 327 (3.41); ν_{max}(KBr)/cm^{-1} 3059, 2955, 1659, 1601, 1555, 1362, 1302, 1148, 1064, 843, 764 and 409; *m/z* 171 (14.6, M + 1), 170 (100, M), 142 (12, M − CO), 116 (35, M − CO − C_2H_2), 114 (96, M − 2CO), 88 (74, M − $C_4H_2O_2$), 63 (30) and 62 (80%).

Attempted demethylation and oxidation of **4** employing iodotrimethylsilylane[11] provided complex product mixtures that, after the removal of iodine ($Na_2S_2O_3$), provided mass spectral evidence for 6-iodomethyl-3,6-dimethoxynaphthalene **5e** formed by opening of the three-membered ring; *m/z* 328 (6, M), 327 (9, M − H), 201 (22, M − I). Separation and purification could not be effected.

Methanolysis of cyclopropa[*b*]naphthalene-3,6-dione 16

Quinone **16** (51 mg, 0.3 mmol) was stirred with silver(I) nitrate (25 mg, 0.15 mmol) in anhydrous methanol (100 cm^3) for 1 h. Work-up as described above for diether **4** gave a yellow solid that was purified by column chromatography. Crystallisation of the product (dichloromethane–light petroleum, 1:3) afforded 6-methoxymethylnaphthalene-1,4-dione (34 mg, 56%) as yellow needles, mp 78–79 °C (lit.,[27] 81–82 °C); δ_H in accord with that previously reported.[27]

Attempted demethylation of the dimethoxy(diphenylmethylidene)cycloproparene 15a

To a solution of **15a** (50 mg, 0.14 mmol) in acetonitrile (20 cm^3) was added dropwise with stirring a solution of cerium(IV) ammonium nitrate (226 mg, 0.412 mmol) in water (5 cm^3). The resultant solution was stirred for a further 30 min and dichloromethane (40 cm^3) added. The lower organic phase was separated, the aqueous layer extracted with dichloromethane (15 cm^3) and the combined organic phases washed, (water, 3 × 50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to an orange–red oil (32 mg). TLC (dichloromethane) indicated two components (R_F 0.70 and 0.82). Radial chromatography (dichloromethane elution) afforded two bands A (R_F 0.82; 9.9 mg) and B (R_F 0.82; 6.1 mg) which have eluded structural identification.

Attempted silylation of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione 16

To a cooled (−70 °C) and stirred solution of **16** (54 mg, 0.32 mmol) in anhydrous THF (10 cm^3) under oxygen-free nitrogen was added dropwise butyllithium in hexanes (0.19 cm^3, 0.32 mmol). The turquoise solution was allowed to warm to −30 °C for 1.5 h, recooled to −70 °C and chlorotrimethylsilane (34 mg, 0.40 mmol) added dropwise and the solution warmed to −30 °C and the lithiation–silylation procedure repeated. The solution was then left to warm to room temperature overnight (16 h). Aqueous $NaHCO_3$ (20 cm^3) was added and the mixture was extracted with light petroleum (3 × 25 cm^3). The combined organic extracts were washed (water, 3 × 20 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to a brown oil (61 mg). The ^1H NMR and mass spectra of the crude product indicated the absence of quinone **16** but no resonances compatible with the disilyl compound **17** were present; significant decomposition was implicated.

Attempted demethylation of the dimethoxydisilylcyclopropparene 14

To a stirred solution of dimethoxycyclopropparene **14** (100 mg, 0.29 mmol) in acetonitrile–dichloromethane (3:2, 10 cm^3) was added portionwise cerium(IV) ammonium nitrate (480 mg, 0.87 mmol) in water (10 cm^3). The addition was carried out so as to minimise, but to observe, a transient blue–black colouration. The resultant orange solution was stirred for a further 30 min, the lower organic phase collected, and the aqueous layer extracted with dichloromethane (2 × 15 cm^3). The combined organic extracts were washed, (water, 3 × 20 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to a claret oil. Column chromatography (3:1 light petroleum–ethyl acetate elution) afforded, as the most mobile yellow band, a product tentatively assigned as 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene-3,6-dione **17** as an orange–red oil (23 mg, 25%), δ_H 0.03 (s, 2 × $SiMe_3$), 6.88 (s, 4/5-H) and 7.47 (s, 2/7-H); *m/z* 315 (1.3), 314 (4.2, M), 299 (3.6, M − Me) and 73 (100, $SiMe_3$). All further attempts using this and modifications of this procedure failed to provide identifiable products.

Single-crystal X-ray diffraction analysis of 1*H*-cyclopropa[*b*]-naphthalene-3,6-dione 16

Crystal data. $C_{11}H_6O_2$, *M* 170.1. Monoclinic, a = 3.779(1), b = 8.066(3), c = 24.920(8) Å, α = 90, β = 91.93(3), γ = 90°, V = 759.1(4) $Å^3$ (by least-squares refinement on diffractometer angles for 50 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (No. 14), Z = 4, D_x = 1.489 g cm^{-3}. Yellow needles; crystal dimensions 0.37 × 0.10 × 0.08 mm^3, μ(Mo-Kα) = 0.10 mm^{-1}.

Data collection and processing.[29] Siemens P4 four circle diffractometer, Wyckoff scan mode with $2\theta_{max}$ = 70°, graphite monochromated Mo-Kα radiation, data collection at 125 K; 3581 unique reflections (no absorption correction was performed) giving 2501 with $F_o \geqslant 4\sigma(F)$.

Structure analysis and refinement. Direct methods with full-matrix least-squares refinement with SHELXTL-Plus (SGI IRIS Indigo) using the implemented atomic scattering factors. All non-hydrogen atoms were given anisotropic and hydrogen atoms isotropic temperature parameters and refined without further constraints. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0003*F_o^2]$ gave satisfactory agreement analyses. Final R and R_w values are 0.0550 and 0.0552.

The X–X difference Fourier map [Fig. 2(*b*)] was produced with the SHELXTL-Plus programme package. The data were provided from a high angle refinement using a weighted scheme with an x-factor of 5.[32] The hydrogen bond distances were expanded from the previously refined positions by 1.008 Å and were fixed with their isotropic temperature factors.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/8.

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