o-Pleiadienequinones. Part 3.[1] Ring Enlargement of *o*-Pleiadienequinones with Diazoalkanes

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The reactions of *o*-pleiadienequinones (**1**) and (**2**) with various diazoalkanes are described. In the absence of catalyst pyrazoline derivatives (**3**) and (**4**) were obtained. In the presence of Lewis acid catalysts ring-enlarged cyclo-octa[*de*]naphthalenones (**5a**), (**6**), and (**7a**) were obtained, achieving syntheses of the first known higher analogues of phenalenone. The reaction of the quinone (**2**) with trimethylsilyldiazomethane gave cyclo-octa[*de*]naphthalenedione (**8**). The physical properties of these compounds are described and the mechanism of formation is discussed. The quinone (**1**) formed 1 : 1 complexes with divalent metal ions.

The reaction of *o*-quinones with diazoalkanes is interesting in that ring enlargement is achieved relatively easily. It is reported that the reaction of acenaphthenequinone with diazoalkanes gave phenalenols in good yield,[2] and the reaction of 1,2-naphthoquinone with diazomethane gave 3,4-benzotropolone.[3] Ring enlargement from a seven-membered ring quinone to an eight-membered ring compound, however, has not yet been reported. We have synthesized *o*-pleiadienequinone (**1**)[1a] and have reported the reactivity of this compound[1b] as part of a study of non-benzenoid quinones containing a seven-membered ring.

We now report that ring enlargement of *o*-pleiadienequinone (**1**) and 9-chloro-*o*-pleiadienequinone (**2**) occurs when they are treated with diazoalkanes. Syntheses of the quinones (**1**) and (**2**) were carried out as described in the literature[1,4] with a slight modification as described in the Experimental section.

The LUMO coefficients of quinone (**1**) were obtained by CNDO/2 MO calculation[5] and are shown in Table 1. The results of this suggest that the molecule is planar with nearly equivalent reactivity towards nucleophilic reagents of the 1-, 3-, 4-, 6-, and 10-positions. Similarly, the 7- and 8-carbonyl carbons would be expected to have similar reactivity. These results contrast with the behaviour of the quinone (**1**) with nucleophilic reagents such as alcohols under acidic conditions when attack occurred solely at the 1, 3, 6, and 8-positions and not at the 4-, 7-, and 10.[1b]

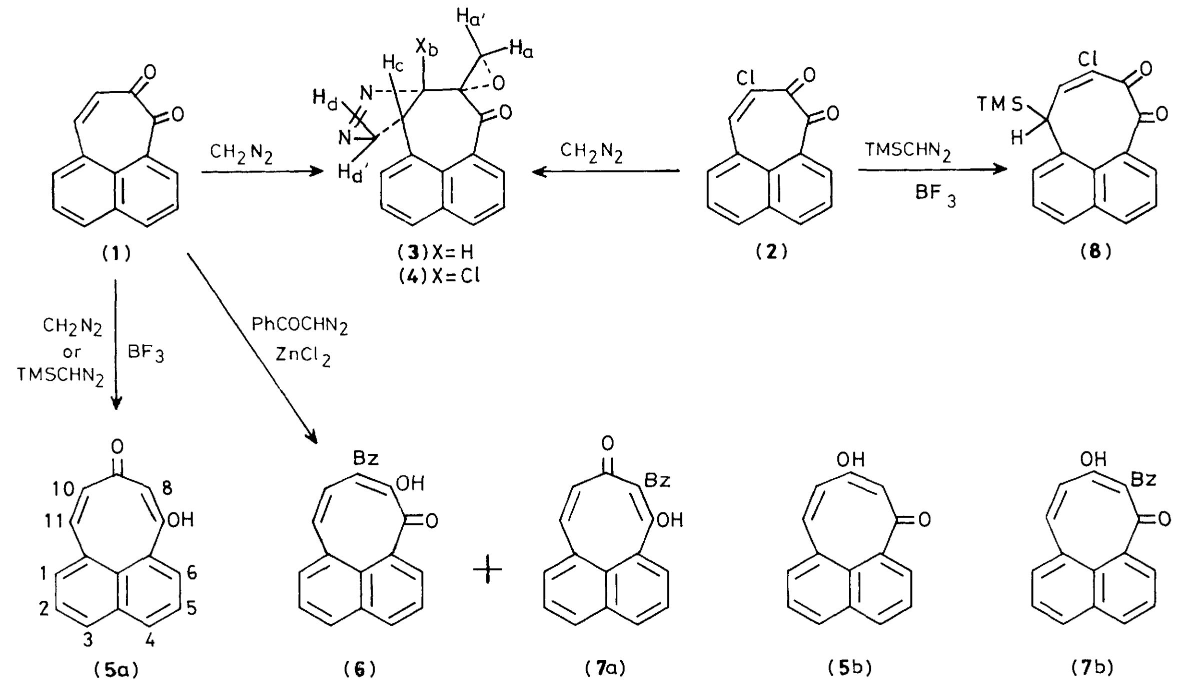
The *o*-quinone (**1**) was allowed to react with a large excess of diazomethane in ether–dichloromethane solution at 3—5 °C for 10 days in a refrigerator to afford the pale yellow pyrazoline derivative (**3**) (19.5%). The presence of a pyrazoline ring was deduced from mass spectral data and elemental analysis. Under similar reaction conditions the chloro quinone (**2**) also afforded a pyrazoline derivative (**4**) (76%). The similarity of these compounds (**3**) and (**4**) was suggested from comparison of their spectral data. The ^{1}H n.m.r. spectrum of compound (**3**) shows a benzylic proton H_c at δ 3.74 as an apparent quartet (J_{bc}=J_{cd}=$J_{cd'}$ 9.7 Hz, determined by decoupling of the protons) and indicating that the direction of addition of diazomethane is regiospecific as shown in Scheme 1. In compound (**4**) the benzylic proton appeared at δ 3.93 as an apparent triplet (J_{cd}=$J_{cd'}$ 9.7 Hz). The absorption maxima of the naphthoyl carbonyl group appear in the i.r. spectrum at 1 680 and 1 681 cm^{-1} for compounds (**3**) and (**4**), respectively. The *syn* or *anti* relation between the pyrazoline and oxirane rings was determined as follows. The lower signal of the oxirane methylene protons appears at δ 3.40 (H_a) in compound (**3**), whereas that of compound (**4**) appears at δ 3.52, showing that in the latter compound the steric effect of the chlorine atom is large enough to force the H_a proton closer to the carbonyl group. This means that the oxirane and the pyrazoline rings are on the *syn* side in the compound (**4**), and therefore also in compound (**3**). This view is supported by consideration of molecular models.

In the presence of boron trifluoride–diethyl ether the reaction of quinone (**1**) with diazomethane in ether solution gave as expected a ring-enlarged compound, cyclo-octa[*de*]-naphthalenol (**5**), (1.2%) as orange crystals with 66.5% recovery of quinone (**1**). This compound was formed by formal insertion of a one-carbon unit between the C-7 and C-8 carbons of quinone (**1**). The same compound (**5**) was also obtained (5.3%) by the reaction of the quinone (**1**) with trimethylsilyldiazomethane in the presence of boron trifluoride–diethyl ether (Scheme 1): $\nu_{max.}$ 3 556 (OH) and 1 719 cm^{-1} (CO). The latter is much higher than that expected for a naphthoyl or α,β-unsaturated carbonyl group, suggesting that the carbonyl group is not co-planar with the naphthalene ring or the α,β-olefinic group. The ^{1}H n.m.r. signal of 10-H appears at δ 6.10 as a doublet with a small coupling constant of $J_{10,11}$ 5.9 Hz and $J_{8,10}$ 1.6 Hz, suggesting that the eight-membered ring is twisted. This is supported by the fact that an aromatic proton at 6-H, which is assumed to be influenced by diamagnetic anisotropy from the carbonyl group at the 7-position, does not appear at as low a field as that of the quinone (**1**). Although the signal of 8-H appears as a broad singlet, decoupling revealed that it is actually coupled with 10-H ($J_{8,10}$ 1.6 Hz) and OH ($J_{OH,8}$ 2.4 Hz). Coupling between OH and 10-H was not observed and the proton of 8-H was not exchangeable with deuterium oxide. ^{13}C N.m.r. showed 14 carbon signals (the signal for one tertiary carbon is hidden). These n.m.r. data showed that in chloroform solution at room temperature compound (**5**) exists in the form (**5a**). However there is no evidence for the possible isomer (**5b**) or of an equilibrium mixture of the two. The signal at δ 205.61 assigned to the carbonyl at C-9 is reasonably interpreted as that of a twisted unsaturated carbonyl group. Interestingly, the i.r. absorption maximum of the carbonyl group at 1 719 cm^{-1} in chloroform solution shifts to 1 700 cm^{-1} in the solid phase (KBr) suggesting that compound (**5**) may have another isomer or conformer.

Reaction of the quinone (**1**) with diazoacetophenone for 17 days at 5 °C gave only recovery of starting material and diazoacetophenone (91.1% and 66.5%, respectively). Upon refluxing the quinone (**1**) with diazoacetophenone in benzene in the presence of anhydrous zinc chloride, two different types of eight-membered ring compounds, (**6**) and (**7**), and chloroacetophenone ($ClCH_2COPh$) were obtained in yields of 11.2,

Table 1. Calculated π-LUMO coefficients of the quinone (**1**) (CNDO/2).[5] Optimised molecular geometry is planar.

Compound (**1**)	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
	−0.299	−0.112	0.309	−0.297	0.112	0.286	−0.234	−0.246
	C-9	C-10	C-3a	C-6a	C-10a	C-10b	O-7	O-8
	−0.219	0.275	−0.006	−0.198	0.215	−0.010	0.373	0.392



Scheme 1.

4.8, and 40%, respectively (Scheme 1). Compounds (**6**) and (**7**) were formed by the formal insertion of a one-carbon unit between C-8 and C-9, and C-7 and C-8 of the quinone (**1**), respectively. The ^{1}H n.m.r. signal of the 10-H of compound (**6**) appears at δ 6.22 as a doublet of characteristic weak coupling ($J_{10,11}$ 6.0 Hz), suggesting that the eight-membered ring of compound (**6**) is twisted as in compound (**5a**). This is supported by the fact that no naphthyl proton is influenced by the carbonyl group and appears at as low a field as that of the quinone (**1**). A signal at δ 3.80 was assigned to one hydroxy group. The ^{13}C n.m.r. spectrum of compound (**6**) shows only the presence of sp^2 carbon atoms, eliminating the possibility of intramolecularly ring-closed structures. The signal at δ 204.9 for the C-7 carbonyl group confirms the twisted carbonyl structure. The i.r. absorption maxima of the hydroxy, the eight-membered-ring- and the naphthoyl-carbonyl groups appear at 3 542, 1 722, and 1 688 cm^{-1} respectively. The last two values are considered to be a result of the influence of the twisted eight-membered ring.

Compound (**7**) shows similar spectral characteristics to those of compound (**6**). The ^{1}H n.mr. spectra show a singlet at δ 3.57 due to one hydroxy group and two doublets at δ 6.23 and δ 7.97 due to 10-H and 11-H respectively. Again the coupling constant, $J_{10,11}$ 5.9 Hz, is as small as that of compound (**6**), suggesting that a twisted 8-membered ring is present. Since the signal appearing at the lowest field is that of 11-H and not an aromatic proton, the structure of the compound is (**7a**) and not (**7b**), in which the influence of the diamagnetic anisotropy from the carbonyl group at the 7-position would be expected to be towards a peri-proton. The ^{13}C n.m.r. spectra showed the presence of 19 carbons (the signals for two carbons are hidden) and no other carbon signal was observed in the neighbouring regions of the eight-membered ring carbonyl at δ 204.83 and the enol carbon at δ 88.73. This confirms the above interpretations. The i.r. spectrum of compound (**7**) in chloroform solution shows absorption maxima at 3 544 cm^{-1} for the hydroxy group, and 1 721 and 1 669 cm^{-1} for the eight-membered-ring- and benzoyl-carbonyl groups respectively. In the solid phase (KBr), however, the absorption of 1 721 cm^{-1} was shifted to 1 710 cm^{-1} and that of 1 669 cm^{-1} split into two maxima at 1 680 and 1 657 cm^{-1}. This indicates that compound (**7**) takes the form of an equilibrium isomer (**7b**) and/or conformer about the benzoyl carbonyl group in the solid phase. A similar but smaller shift of the i.r. absorption maximum of 1 722 cm^{-1} ($CHCl_3$) to 1 716 cm^{-1} (KBr) of compound (**6**) was observed. Reaction of the quinone (**1**) with phenyldiazomethane at 5 °C for 12 days or at 0 °C for 6 h and room temperature overnight in the presence of anhydrous zinc chloride afforded benzaldehyde azine (71.1 or 76.3% respectively); no quinone (**1**) was recovered. Upon refluxing quinone (**1**) with ethyl diazoacetate in benzene–ether for 9 days or for 18 h in the presence of anhydrous zinc chloride, gave only recovery of unchanged quinone (**1**) or a mixture of unidentifiable compounds.

Reaction of the 9-chloro quinone (**2**) with trimethylsilyldiazomethane in the presence of boron trifluoride–diethyl ether afforded a colourless eight-membered ring compound (**8**) (16.0%). Here the formal ring expansion has occurred between C-10 and C-10a of the quinone (**1**) (Scheme 1). The i.r. spectrum showed an absorption maximum at 1 680 cm^{-1} (KBr) assigned to two carbonyl groups. The ^{1}H n.m.r. spectrum of compound (**8**) showed the following signals: δ 0.25 (9 H, s, trimethylsilyl H),

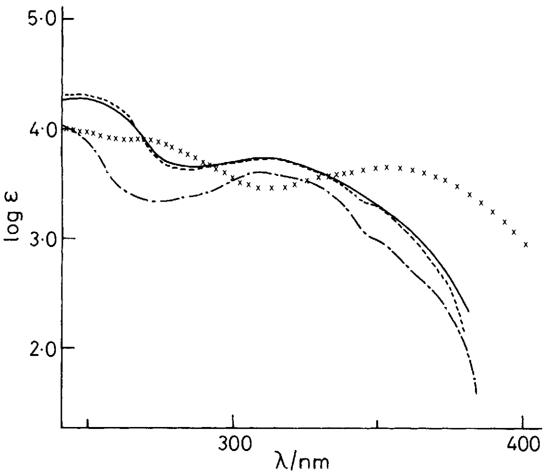
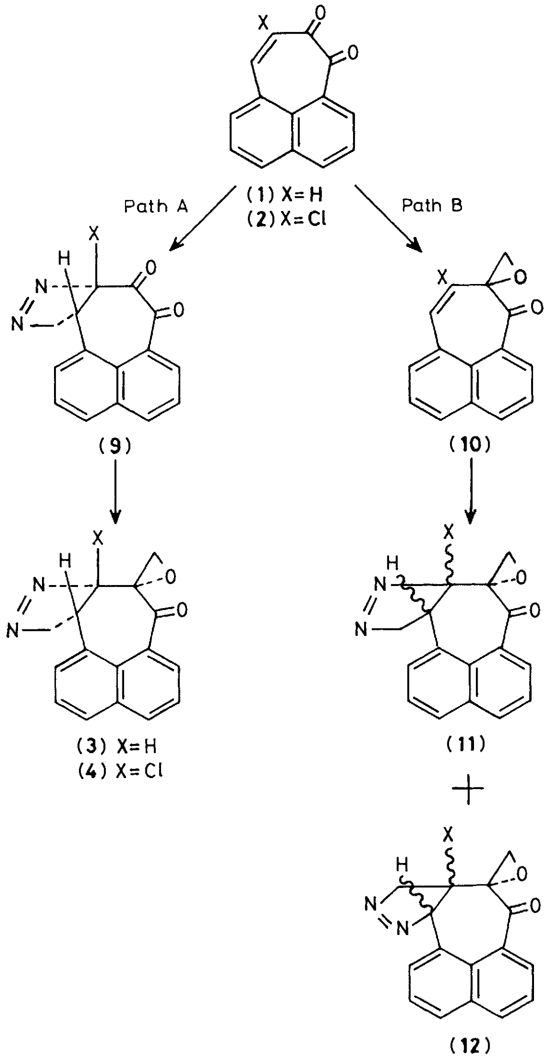


Figure. Electronic spectra of cyclo-octa[*de*]naphthalen-ones and -dione: – – – – – ketone (5); - - - - - - - - ketone (6); ——— ketone (7); × × × × × × × × × (8) (solution in chloroform).



Scheme 2.

7.22 (d, $J_{10,11}$ 12.1 Hz, olefinic 10-H), and 3.95 (d, $J_{10,11}$ 12.1 Hz aliphatic 11-H). Here again the chemical shift of the aromatic protons was not influenced by magnetic anisotropy from the carbonyl group at the 7-position. The ^{13}C n.m.r. spectrum of compound (**8**) showed two carbonyl carbon signals at δ 187.3 and 201.2, confirming the proposed structure.

The electronic spectra of compounds (**5a**), (**6**), (**7a**), and (**8**) are shown in the Figure. Those of (**5a**), (**6**), and (**7**) which were unchanged or going from alkaline to acid solution (0.1M) are similar and suggest a structural similarity. That of (**8**) differs and suggests a structural divergence. All the compounds were negative to colour test with iron (III) chloride, supporting the view that the hydroxy groups present are neutral and non-phenolic.

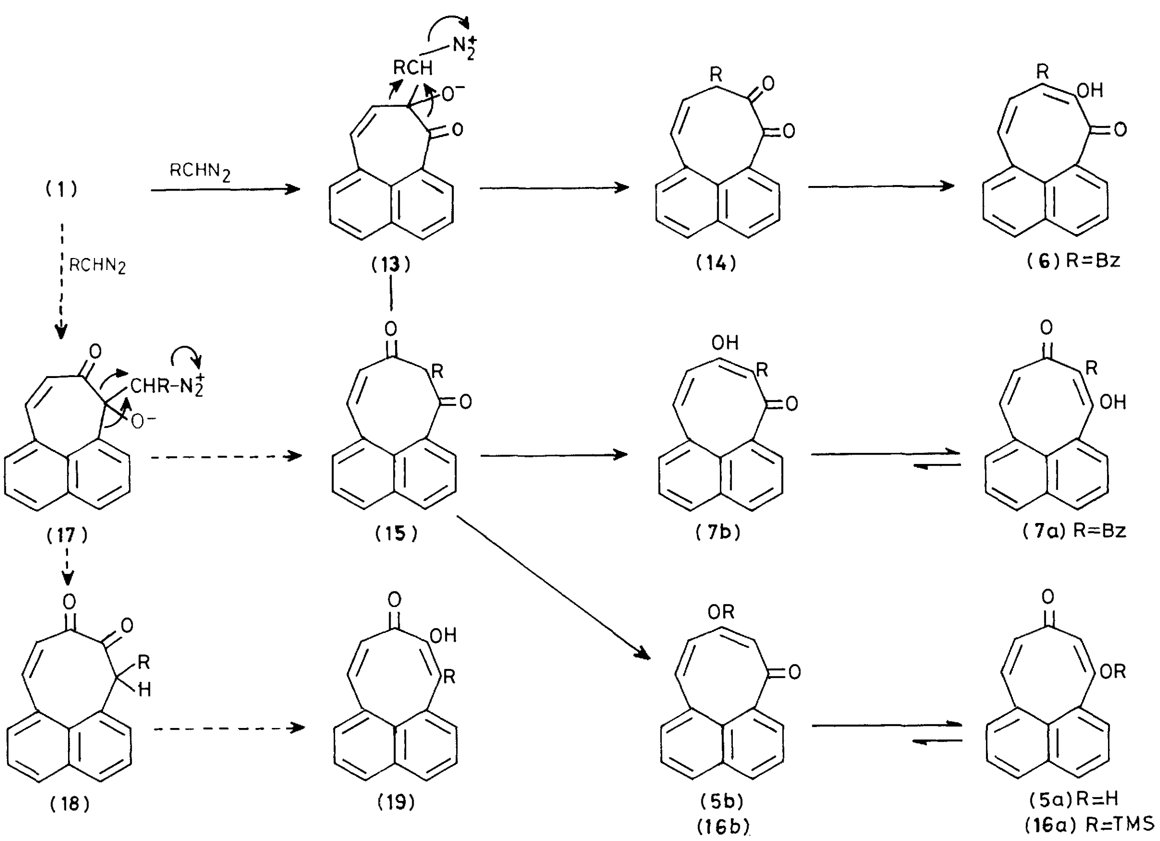
As regards the mechanism of formation of the pyrazoline derivatives (**3**) and (**4**), the first and regiospecific cycloaddition of diazomethane to the quinones (**1**) and (**2**) can be explained well with the HOMO (diazomethane)-LUMO (quinone) overlapping (Scheme 2). The second addition of diazomethane to the carbonyl group situated next to the pyrazoline ring of the intermediate (**9**) would occur from the less sterically hindered side to form compounds (**3**) and (**4**) as shown by path A. If the reverse sequence of addition were possible, the second addition of diazomethane to the first formed oxirane (**10**) would not be regioselective and would produce the pyrazolines (**11**) and/or (**12**). The experimental facts contradict this assumption and therefore path B is unacceptable.

The mechanism of the formation of the eight-membered-ring compounds can be considered as shown in Scheme 3. Diazoalkane attack at C-8 of the less hindered carbonyl group of quinone (**1**) is co-ordinated by divalent metal ion or trivalent borane to form an intermediate (**13**), from which C-7 carbon migrates onto the carbon next to the diazo group in concert with elimination of nitrogen to afford the 7,9-diketone (**15**). If the substituent group R of the intermediate (**15**) is COPh or hydrogen, enolization of the diketone (**15**) gives compound (**7**) or (**5**) respectively.

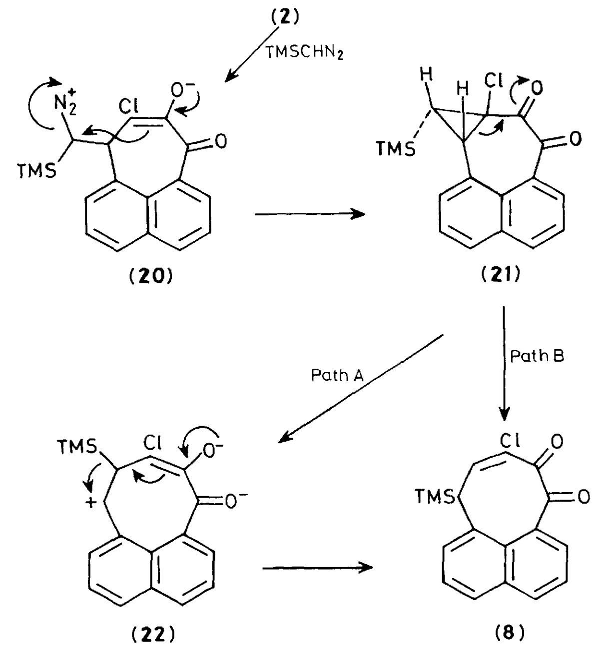
If the substituent group R of the intermediate (**15**) is trimethylsilyl (TMS), migration of this onto oxygen is preferred to that of hydrogen and the silyl enol ether (**16**) is formed which is then hydrolysed to give compound (**5**). If R is the COPh group, migration of C-9 from intermediate (**13**) affords the 7,8-diketone (**14**), which is enolized to afford compound (**6**). A less probable mechanism is that diazomethane attacks at the more hindered carbonyl carbon (C-7) than that (C-8) of the quinone (**1**) to form an intermediate (**17**), which is similarly converted into intermediates (**15**) and (**18**). However, as described previously, formation of a 8,9-dioxo compound like (**18**) or (**19**) was not observed and formation of compound (**6**) cannot be explained.

The mechanism of the reaction between the 9-chloro quinone (**2**) and trimethylsilyldiazomethane is shown in Scheme 4. At first trimethylsilyldiazomethane attacks at C-10 to form the intermediate (**20**), which rearranges to form the three-membered ring compound (**21**) with simultaneous elimination of nitrogen. The relative configuration between the TMS group and the chlorine atom would be *trans* because of their steric repulsion. From the presumed resulting intermediate (**21**) two paths are possible to form the dione (**8**). Path A is an ionic mechanism, in which the carbonyl-conjugated three-membered ring opens to form the cation (**22**) and the TMS group then migrates to the benzylic cation centre in order to release the steric compression between the TMS group and the chlorine atom to form the dione (**8**). Path B is the concerted mechanism which follows the Woodward–Hoffmann rule[6] or Fukui's frontier orbital molecular theory.[7]

The quinone (**1**) forms 1:1 orange and 1:1 red crystalline complexes with zinc chloride and copper(II) chloride in acetic acid–hexane, and in acetone, respectively. The former has an i.r. absorption maximum at 1 639 cm^{-1} for the carbonyl group and the latter 1 622 cm^{-1}, each of which is shifted from the quinone position by 21 and 38 cm^{-1} respectively. Both of them could be dissolved in nonpolar solvents with difficulty but decomposed in polar solvents.



Scheme 3.



Scheme 4.

Experimental

M.p.s. were determined with a Mitamura air-bath apparatus and are not corrected. ^1H and ^{13}C N.m.r. spectra (tetramethylsilane as internal standard) were determined with a Jeol-JNM-FX90Q (90 MHz) and a Bruker AM 400 (400 MHz) spectrometer. I.r. spectra were determined with a Hitachi 270-50 instrument, electronic spectra (u.v. and vis.) with a Hitachi 340 spectrophotometer, and mass spectra with a Jeol-01SG-2 spectrometer. Unless otherwise stated the spectra were taken in the following solvents/media: u.v. and visible, $CHCl_3$; i.r., $CHCl_3$; ^1H and ^{13}C n.m.r., $CDCl_3$. The progress of most reactions was followed by t.l.c. using Kieselgel 60 G (Merck). Preparative column chromatography was carried out using Kieselgel 60 (Merck 70—230 mesh). Ether refers to diethyl ether.

Spiro{*naphtho*[1′,8′:4,5,6]*cyclohepta*[1,2-c]*pyrazole*-8,2′-*oxiran*}-7(8H)-*one* (**3**).—To a solution of diazomethane (17.4 mmol) in ether (90 ml) was added portionwise a solution of the quinone (**1**) (800 mg, 3.84 mmol) in dichloromethane (100 ml) at 0 °C. The reaction mixture was kept in a refrigerator for 10 days after which solvent was removed at room temperature and the residue chromatographed successively on a silica gel column and a Lobar column (Lichroprep Si 60, Merck) with dichloromethane as eluant to give the *title compound* (**3**) (177 mg, 19.5%) as pale yellow needles, m.p. 168—169 °C (decomp.) (from benzene–hexane) (Found: C, 72.4; H, 4.4; N, 10.45. $C_{16}H_{12}N_2O_2$ requires C, 72.71; H, 4.54; N, 10.59%) *m/z* (20 eV) 265 ($M^{+\cdot}$ + 1, 1.0%), 264 ($M^{+\cdot}$, 3.5), 236 ($M^{+\cdot}$ – CO and/or $M^{+\cdot}$ – N_2, 3.5), 235 ($M^{+\cdot}$ – CHO, 32), 207 ($M^{+\cdot}$ – CHO–N_2 and/or $M^{+\cdot}$ – CHO–CO, 44), 178 ($M^{+\cdot}$ – CO–CH_2O–N_2, 100), and 165 ($C_{13}H_9^+$, 78); $\lambda_{max.}$ 252 (log ε 4.12) and 328 nm (3.81); $\nu_{max.}$(KBr) 1 680 cm^{-1}; δ_H(200 MHz) 3.10 (1 H, d, $J_{aa'}$ 4.4 Hz, $H_{a'}$), 3.40 (1 H, d, $J_{aa'}$ 4.4 Hz, H_a), 3.74 (1 H, q, J_{bc}=$J_{cd'}$ 9.7 Hz, H_c), 4.31 (1 H, ddd, J_{cd}=$J_{cd'}$ 9.7 Hz, J_{bd} 2.2 Hz, H_d), 4.93 (1 H, dd, $J_{cd'}$ 9.7 Hz, $J_{dd'}$ 18.0 Hz, $H_{d'}$), 5.15 (1 H, dd, J_{bc} 9.7 Hz, J_{bd} 2.2 Hz, H_b), and 7.23—8.09 (6 H, m, ArH); δ_C(50 MHz) 44.3, 50.9, 62.3 (q), 82.0, 94.7, 125.2, 126.6, 128.8 (q), 129.4, 129.7, 132.2, 132.5 (q), 133.7 (q), 135.1 (q), 135.1, and 195.1 (C=O).

7-*Hydroxycyclo-octa*[de]*naphthalen*-9-*one* (**5a**).—(a) To a stirred mixture of the quinone (**1**) (800 mg, 3.84 mmol), boron trifluoride–diethyl ether (830 mg, 5.53 mmol), and dichloromethane (110 ml) at 0 °C under nitrogen, a solution of diazomethane (18.0 mmol) in ether (120 ml) was added over 30 min. The reaction mixture was stirred for a further 6 h and kept in a refrigerator for 18 h. The reaction mixture was diluted with water (500 ml) and filtered. The filtrate was extracted with dichloromethane and the organic layer washed with brine, dried ($MgSO_4$), and evaporated and the residue chromatographed on a silica gel column with dichloromethane as eluant to give recovery of the quinone (**1**) (532 mg, 66.5%) and the *title compound* (**5a**) (10 mg, 12%) as orange crystals, m.p. 142—144 °C (from benzene–hexane after purification by h.p.l.c. (Found: C, 80.85; H, 4.5. $C_{15}H_{10}O_2$ requires C, 81.07; H, 4.54%); *m/z* (75 eV) 224 ($M^{+\cdot}$ + 2, 2.7%), 223 ($M^{+\cdot}$ + 1, 12.7), 222 ($M^{+\cdot}$, 67.3), 205 ($M^{+\cdot}$ − OH, 1), 194 ($M^{+\cdot}$ − CO, 22), 168 ($M^{+\cdot}$ − C_2H_2–CO, 42), and 165 ($C_{13}H_{19}^+$, 100); $\lambda_{max.}$ 307 nm (log ε 3.63); $\nu_{max.}$ 3 556 (OH) and 1 719 (C=O), $\nu_{max.}$(KBr) 3 402 and 1 700 cm^{-1}; δ_H(400 MHz) 3.40 (1 H, s, OH), 4.71 (1 H, br s, 8-H), 6.10 (1 H, dd, $J_{10,11}$ 5.9 Hz, $J_{8.10}$ 1.6 Hz, 10-H), 7.76 (1 H, m, 11 H), and 7.49—7.84 (6 H, m, ArH); δ_C(100 MHz) 85.53 (HO–C), 120.57, 121.55, 124.77, 126.63, 128.26, 128.64, 130.24, 131.52 (q), 135.65 (q), 139.12 (q), 140.09 (q), 162.20, and 205.61 (C=O).

(b) To a stirred mixture of quinone (**1**) (800 mg, 3.84 mmol), boron trifluoride–diethyl ether (830 mg, 5.53 mmol), and dichloromethane (20 ml) at −40 to −35 °C under nitrogen was added a 10% solution of trimethylsilyldiazomethane in hexane (6.58 mg, 5.76 mmol) during 20 min. After 3 h of further stirring at −30 °C the reaction mixture was mixed with ice–water (20 ml) and stirred for 1 h. The mixture was filtered to remove any black material, the filtrate extracted with dichloromethane, and the organic layer washed with brine, dried ($MgSO_4$), and evaporated. The residue was purified by silica gel column chromatography, preparative t.l.c., and h.p.l.c. (silica gel), with dichloromethane as eluant to give the pure compound (**5a**) (45 mg, 5.27%) and recovery of the quinone (**1**) (193 mg, 24.1%).

6-Benzoyl-8-hydroxycyclo-octa[de]*naphthalen-7-one* (**6**) *and 8-Benzoyl-7-hydroxycyclo-octa*[de]*naphthalen-9-one* (**7a**).—(a) To a stirred benzene solution (50 ml) of diazoacetophenone (1.70 g, 11.6 mmol) at room temperature under nitrogen, were added the quinone (**1**) (800 mg, 3.84 mmol) portionwise and anhydrous zinc chloride (0.75 g, 5.50 mmol). The reaction mixture was stirred for 40 h and then heated under reflux for 24 h; after this it was poured into 2M HCl and the benzene layer separated and washed with water. The aqueous layer was extracted with dichloromethane, the extract washed with water, and the two organic layers combined, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column with dichloromethane as eluant to afford 2-chloroacetophenone (720 mg, 40.0%) as colourless plates, m.p. 52.5—53.5 °C (from hexane, lit.[8], 56.5 °C) (Found: C, 62.1; H, 4.6. Calc. for C_8H_7ClO: C, 62.15; H, 4.56%); $\nu_{max.}$(KBr) 1 701 cm^{-1} (C=O); δ_H(90 MHz) 4.71 (2 H, s, CH_2), and 7.44—7.97 (5 H, m, ArH); the *title compound* (**6**) (140 mg, 11.2%) as colourless prisms, m.p. 144.0—145.5 °C (from benzene after repeated column chromatography on a silica gel with benzene–dichloromethane as eluant) (Found: C, 81.15; H, 4.45. $C_{22}H_{14}O_3$ requires C, 80.97; H, 4.32%); *m/z* (70 eV) 328 ($M^{+\cdot}$ + 2, 0.5%), 327 ($M^{+\cdot}$ + 1, 4), 326 ($M^{+\cdot}$, 16), 308 ($M^{+\cdot}$ − H_2O, 4), 281 ($M^{+\cdot}$ − CO–OH, 29), 221 ($M^{+\cdot}$ − PhCO, 38), 204 ($M^{+\cdot}$ − PhCO–OH, 61), 165 ($C_{13}H_9^+$, 70), and 105 ($PhCO^+$, 100); $\lambda_{max.}$ 243 (log ε 4.33) and 306 nm (3.76); $\nu_{max.}$ 3 542 (OH), 1 722 (C=O), and 1 668 cm^{-1} (C=O), $\nu_{max.}$(KBr) 3 428, 1 716, and 1 666 cm^{-1}; δ_H(400 MHz) 3.80 (1 H, s, OH), 6.22 (1 H, dd, $J_{10,11}$ 6.0 Hz, *J* 1.2 Hz, 10-H), 7.06—8.00 (11 H, m, ArH), and 7.96 (1 H, dd, $J_{10,11}$ 6.0 Hz, *J* 1.2 Hz); δ_C (22.5 MHz) 88.9 (HO–C), 121.3, 122.9, 125.5, 126.8, 127.8, 128.3, 128.6, 129.1, 129.7, 131.6 (q), 132.6 (q), 134.9 (q), 136.1 (q), 139.5 (q), 141.1 (q), 163.4, 167.8 (C=O), and 204.9 (C=O); and the *title compound* (**7a**) (60 mg, 4.78%) as colourless needles, m.p. 158—159 °C [from benzene–hexane after repeated chromatography on a silica gel column, preparative t.l.c., and h.p.l.c. (silica gel) with dichloromethane as eluant] (Found: C, 81.25; H, 4.5. $C_{22}H_{14}O_3$ requires C, 80.97; H, 4.32%); *m/z* (70 eV) 328 ($M^{+\cdot}$ + 2, 1.0%), 327 ($M^{+\cdot}$ + 1, 4.0), 326 ($M^{+\cdot}$, 16), 308 ($M^{+\cdot}$ − H_2O, 5), 281 ($M^{+\cdot}$ − CO–OH, 33), 221 ($M^{+\cdot}$ − PhCO, 39), 204 ($M^{+\cdot}$ − PhCO–OH, 69), 165 ($C_{13}H_9^+$, 82), and 105 ($PhCO^+$, 100); $\lambda_{max.}$ 242 (log ε 4.32) and 307 nm (3.77); $\nu_{max.}$ 3 544 (OH), 1 721 (C=O), and 1 669 cm^{-1} (C=O); $\nu_{max.}$(KBr) 3 424, 1 710, 1 680, and 1 657 cm^{-1}; δ_H(400 MHz) 3.57 (1 H, s, OH), 6.23 (1 H, d, *J* 5.9 Hz, 10-H), 7.11—7.98 (12 H, m, ArH), and 7.97 (1 H, d, *J* 5.9 Hz, 11-H), with the exception of one hydroxy proton no exchangeable proton with D_2O was observed; δ_C(100 MHz) 88.73 (HO–C), 121.41, 122.84, 125.71, 127.04, 127.97, 128.48, 128.50, 129.22, 129.75, 131.67 (q), 132.88, 134.88 (q), 135.94 (q), 139.37 (q), 141.02 (q), 190.92, 197.52 (C=O), and 204.83 (C=O).

(b) A mixture of the quinone (**1**) (800 mg, 3.84 mmol), diazoacetophenone (1.70 g, 11.6 mmol), ether (100 ml), and dichloromethane (100 ml) was kept in a refrigerator for 17 days. After removal of the solvent on a rotary evaporator, the residue was chromatographed on a silica gel column with dichloromethane as eluant to give recovery of diazoacetophenone (1.13 g, 66.5%) and the quinone (**1**) (769 mg, 96.1%).

Reaction of the Quinone (**1**) *with Phenyldiazomethane.*—(a) To a chilled and stirred solution of the quinone (**1**) (800 mg, 3.84 mmol) and benzene (40 ml), was added phenyldiazomethane [obtained by the oxidation of benzaldehyde hydrazone (37.7 mmol) with mercury (II) chloride] and the reaction mixture was kept in a refrigerator for 12 days. After removal of the solvent at room temperature, the residue was purified by silica gel column chromatography with dichloromethane as eluant to give benzaldehyde azine (2.97 g, 71.1%) as yellow needles, m.p. 90.0—92.0 °C (from methanol). This was identified by comparison of the mixed melting point and spectral data with an authentic sample (m.p. 92—93 °C) synthesized by another route.[9]

(b) To a stirred mixture of the quinone (**1**) (800 mg, 3.84 mmol), anhydrous zinc chloride (1.00 g, 7.34 mmol), anhydrous ether (20 ml), and benzene (10 ml) at 0 °C under nitrogen was added dropwise during 10 min phenyldiazomethane derived from benzaldehyde (37.7 mmol) as above. The reaction mixture was stirred for a further 6 h at 6 °C and overnight at room temperature. To this reaction mixture was added water (50 ml) and the usual work-up as above gave only benzaldehyde azine (2.99 g, 76.3%).

Reaction of the Quinone (**1**) *with Ethyl Diazoacetate.*—(a) To a stirred mixture of the quinone (**1**) (500 mg, 2.40 mmol) and benzene (25 ml), was added ethyl diazoacetate (978 mg, 8.58 mmol) in ether (6 ml) under nitrogen. The reaction mixture was refluxed for a further 9 days after which the solvent was removed and the residue chromatographed on a silica gel column with dichloromethane as eluant to give recovery of the quinone (**1**) (201 mg, 40.2%).

(b) To a mixture of anhydrous ether (10 ml) and anhydrous zinc chloride (440 mg, 3.23 mmol) was added the quinone (**1**) (500 mg, 2.40 mmol) in benzene (30 ml) under nitrogen. To this stirred orange suspension was added dropwise during 30 min ethyl diazoacetate (1.76 g, 15.4 mmol) in ether (12 ml). The reaction mixture was stirred for 3.5 h and then refluxed for a further 8 h. It was then poured into 2M HCl (60 ml). Work-up gave no identifiable products.

9-Chlorospiro{*naphtho*[1′,8′:4,5,6]*cyclohepta*[1,2-c]*pyrazole-*

8,2′-oxiran}-7(8H)-*one* (**4**).—To a stirred mixture of the chloro quinone (**2**) (800 mg, 3.29 mmol) and dichloromethane (100 ml) was added diazomethane (31.5 mmol) in ether solution (150 ml) slowly at 0 °C. The reaction mixture was kept in a refrigerator for 10 days after which the solvent was removed. The pale yellow residue was chromatographed on a silica gel column with dichloromethane as eluant to give the *title compound* (**4**) (747 mg, 76.0%) as colourless plates, m.p. 158—162 °C (decomp.) (from hexane) (Found: C, 64.4; H, 3.6; N, 9.4. $C_{16}H_{11}ClN_2O_2$ requires C, 64.33; H, 3.71; N, 9.38%); *m/z* (70 eV) 300 ($M^{+\cdot}$ + 2, 0.1%), 299 ($M^{+\cdot}$ + 1, 0.1), 298 ($M^{+\cdot}$, 0.2), 269 ($M^{+\cdot}$ – CHO, 6), 235 ($M^{+\cdot}$ – N_2–^{35}Cl and/or $M^{+\cdot}$ – CO–^{35}Cl, 93), and 165 ($C_{13}H_9^+$, 100); $\nu_{max.}$(KBr) 1 681 cm^{-1}; δ_H(90 MHz) 2.95 (1 H, d, $J_{aa'}$ 4.6 Hz, $H_{a'}$), 3.52 (1 H, d, $J_{aa'}$ 4.6 Hz, H_a), 3.93 (1 H, t, J_{cd}=$J_{cd'}$ 9.7 Hz, H_c), 4.49 (1 H, dd, J_{cd} 9.7 Hz, $J_{dd'}$ 18.2 Hz, H_d), 5.12 (1 H, dd, $J_{cd'}$ 9.7 Hz, $J_{dd'}$ 18.2 Hz, $H_{d'}$), and 7.46—8.13 (6 H, m, ArH); δ_C(22.5 MHz) 48.7, 55.0, 63.5 (q), 83.0, 108.9 (Cl–C), 125.3, 126.7, 128.2 (q), 129.0 (q), 129.5, 130.1, 132.9 (q), 133.2, 134.7 (q), 135.3, and 193.7 (C=O)

9-*Chloro-7-trimethylsilylcyclo-octa*[de]*naphthalene-10,11*(7H)-*dione* (**8**).—To a stirred mixture of the chloro quinone (**2**) (740 mg, 3.05 mmol), boron trifluoride–diethyl ether (659 mg, 4.64 mmol), and dichloromethane (25 ml) was added trimethylsilyldiazomethane (10%; 5.24 g, 4.58 mmol) in hexane solution at –25 to –20 °C under nitrogen during 15 min. The reaction mixture was stirred for 6 h at 0 °C, diluted with dichloromethane (150 ml), and poured into ice–water. The solution was stirred for 30 min, filtered to remove any black precipitate, and the organic layer washed with brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel column with dichloromethane as eluant to give the title compound (**8**) (150 mg, 16.0%) as yellow subliming prisms, m.p. 172—174 °C (from hexane) (Found: C, 65.95; H, 5.25. $C_{18}H_{17}ClO_2Si$ requires C, 65.74; H, 5.21%); *m/z* (70 eV) 330 ($M^{+\cdot}$ + 2, 1.0%), 329 ($M^{+\cdot}$ + 1, 1.5), 328 ($M^{+\cdot}$, 4), 300 ($M^{+\cdot}$ – CO, 5), 293 ($M^{+\cdot}$ – ^{35}Cl, 15), 165 ($C_{13}H_9^+$, 9), and 105 (TMS$^+$, 100); $\lambda_{max.}$ 262sh(log ε 3.95) and 352 nm (3.69); $\nu_{max.}$(KBr) 1 680 cm^{-1}; δ_G(90 MHz) 0.25 (9 H, s, TMS), 3.95 (1 H, d, $J_{10,11}$ 12.1 Hz, 11-H), 7.22 (1 H, d, $J_{10,11}$ 12.1 Hz, 10-H), and 7.36—8.10 (6 H, m, ArH); δ_C(22.5 MHz) – 1.9 (TMS–C), 36.6 (C-11), 125.8, 126.4, 127.5, 128.9, 129.5, 129.7 (q), 131.5 (q), 133.5 (q), 133.8 (q), 134.1, 134 (q), 147.6, 187.3 (C=O), and 201.2 (C=O).

Complexes of the Quinone (**1**).—(a) To a mixture of the quinone (**1**) (50 mg, 0.24 mmol) and glacial acetic acid (1 ml) was added a mixture of anhydrous zinc chloride (60 mg, 0.44 mmol) in glacial acetic acid (1 ml) and hexane (1 ml) to give the *complex compound* as an orange powder (25 mg, 15%), m.p. 145—160 °C (decomp.) (Found: C, 47.95; H, 2.75. $C_{14}H_8Cl_2O_2Zn{\cdot}0.5CH_3CO_2H$ requires C, 48.11; H, 2.69%); $\nu_{max.}$(KBr) 1 639br cm^{-1}.

(b) To a mixture of the quinone (**1**) (50 mg, 0.24 mmol) and acetone (5 ml) was added a mixture of copper(II) chloride dihydrate (45 mg, 0.26 mmol) and acetone (5 ml) to afford the *complex compound* (20 mg, 23%) as red crystals, m.p. 120—150 °C(decomp.) (Found: C, 48.85; H, 2.45. $C_{14}H_8Cl_2CuO_2$ requires C, 49.07; H, 2.44%); $\nu_{max.}$(KBr) 1 622 cm^{-1}.

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References

1 (*a*) J. Tsunetsugu, M. Kanda, M. Takahashi, K. Yoshida, H. Koyama, K. Shiraishi, Y. Takano, M. Sato, and S. Ebine, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1465; (*b*) J. Tsunetsugu, T. Yamaguchi, S. Ebine, and K. Morinaga, *ibid.*, 1986, 1965.

2 B. Eistert and A. Schönberg, *Chem. Ber.*, 1962, **95**, 2416; B. Eistert and H. Selzer, *ibid.*, 1963, **96**, 314.

3 M. Sato, J. Tsunetsugu, and S. Ebine, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 638.

4 R. Gleiter and W. Dobler, *Chem. Ber.*, 1985, **118**, 4725.

5 S. Kumakura and T. Kodama, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2339; molecular geometry was optimized with respect to the CNDO/2 energy by using a modified program of the GEOMIN in QCPE for performing on a HITAC M-280H computer at the Computer Centre of the University of Tokyo.

6 R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395; R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.

7 K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722; K. Fukui, *Acc. Chem. Res.*, 1971, **4**, 57.

8 M. Perrier, *J. Am. Chem. Soc.*, 1947, **69**, 3148.

9 H. H. Hatt, *Org. Synth.*, Coll. Vol. 2, 1943, 395.

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