Adducts from Quinones and Diazoalkanes. Part 10.[1] 2-Diazopropane and 2-Methyl-1,4-naphthoquinone; Structures and Conformations of Novel Vinylic Quinones and Epoxides

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2-Diazopropane and 2-methyl-1,4-naphthoquinone combine to give 3a,9a-dihydro-3,3,9a-trimethylbenz[*f*]indazole-4,9(3*H*)-dione (**1**) which reacts further with 2-diazopropane to give 3a,9a-dihydro-3,3,3',3',9a-pentamethylspiro[9*H*-benz[*f*]indazole-9,2'-oxirane]-4(3*H*)-one (**15**) with unusual ease. Standard methods failed to determine the structure of this compound, but a novel combination of ^{13}C-{^1H-selective} and ^1H-{^1H} nuclear Overhauser enhancement experiments conducted using difference techniques established both the structure and the conformation. The normal adduct (**1**) differs from lower homologues in its stability to acetate ion in methanol, but potassium hydroxide induces loss of nitrogen and the formation of 2-isopropenyl-3-methyl-1,4-naphthoquinone (**7**); if not isolated promptly this reacts further with alkali to give 3,3'-di-isopropenyl-2,2'-ethylenedi-1,4-naphthoquinone (6a). At lower concentrations of alkali the adduct (**1**) forms an intermediate carbanion that traps oxygen to afford 2-isopropenyl-3-methyl-1,4-naphthoquinone 2,3-epoxide (**14**). All these reactions are of types new in this series. The adduct (**3**) from 2-t-butyl-1,4-naphthoquinone and 2-diazopropane is so hindered that it does not react even with potassium hydroxide.

2-Diazopropane is recognised as one of the more reactive (nucleophilic) diazoalkanes;[2] accordingly, we find that it adds instantly to 2-methyl-1,4-naphthoquinone to give the pyrazole derivative (**1**)* at 0 °C. As will appear, the reaction can be decelerated by using a lower temperature but a second product is formed at the same time. The new adduct (**1**) closely resembles its lower homologues described previously.[1,3] The two methyl groups at position 3 afford bands in the ^1H n.m.r. spectrum (Table 1) at widely different fields which can only be explained if one lies over the neighbouring carbonyl group so as to be shielded by it, and this arrangement is possible only if the rings are *cis*-fused just as in simpler examples.

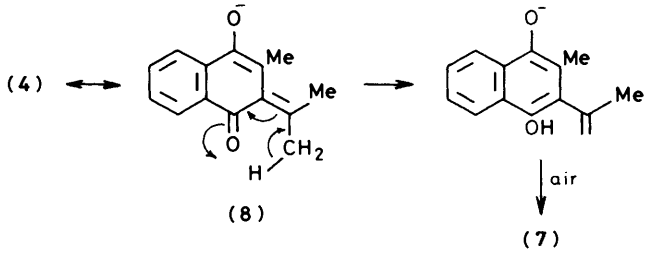
Unlike the lower homologues, the adduct (**1**) is unaffected by sodium acetate in methanol, from which it seems that the proton at position 3a is hindered. We find a similar resistance in the adduct (**2**) from 2-t-butyl-1,4-naphthoquinone and diazomethane, while the much more severely hindered adduct (**3**) from 2-t-butyl-1,4-naphthoquinone and 2-diazopropane fails to react, not only with sodium acetate but even with potassium hydroxide in methanol. These more hindered pyrazoline derivatives also have some thermal stability for we have observed molecular ions for the first time in studying the mass spectra of such adducts by the electron-impact method.

When adducts from diazomethane or diazoethane react with base they lose nitrogen and turn red because of the formation of carbanions that persist long enough to form oxidative dimers (ethylenediquinones).[1,3] The new adduct (**1**) behaves in the same way with potassium hydroxide in methanol and liberates nitrogen and turns red; presumably the carbanion (**4**) is produced, but the derived ethylenebiquinone (**5**) fails to appear. Of course, it would be very hindered. Instead, a dimer (**6a**) is produced by a sequence new in this work. Unsaturation has been introduced, and the carbanionic centre has migrated from the isopropyl group to the quinone methyl group. Since potassium hydroxide is known to convert 2-isopropyl-3-methyl-1,4-naphthoquinone into the similar dimer[4] (**6b**) were concluded that dimer (**6a**) had been formed from the simpler quinone (**7**), and by quenching the reaction mixture with acetic anhydride almost immediately after adding alkali we isolated this quinone in 34% yield. We think that this compound is produced because the carbanion (**4**), which can also be regarded as the oxyanion (**8**), has the correct stereochemistry for a hydrogen shift as shown (Scheme 1) that also effects aromatisation and would not be readily reversible. In agreement, the products do not incorporate any deuterium when the reactions are conducted in dueteriomethanol (CH_3OD) containing potassium deuterioxide.

Table 1. ^1H N.m.r. spectra[a] (at 220 MHz) of dihydrobenzindazolediones

Compd.	Assignments							
	3-H	3a-H	5-, 8-H	6-, 7-H	3-Me	9a-Me	Bu^t	3'-Me
(1)		2.73	8.10m	7.83m	0.91, 1.77	1.83		
(2)	4.26dd,[b] 5.19dd	3.32t[b]	8.03m	7.78m			1.11	
(3)		2.96	8.05m	7.78m	0.86, 1.78		1.06	
(15)		2.37	7.88, 7.55	7.46, 7.61	1.22, 1.83	1.66		0.96, 1.54

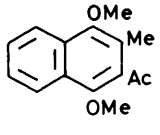
[a] In $CDCl_3$ with tetramethylsilane as internal reference; δ scale. All relative intensities were appropriate to the assignments. [b] AMX Spin system: J_{AM} 18; J_{AX} 10; J_{BM} 10 Hz; first-order analyses only.



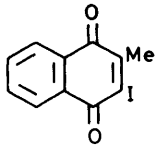
Scheme 1.

* This and other structures represent racemates.

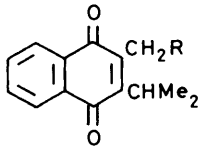
The structures of the vinylic quinone (**7**) and the derived dimer (**6**) were confirmed by ^{1}H n.m.r. spectroscopy (Table 2) and other standard methods. Nevertheless, the compounds seem more stable than expected (simple vinylic quinones are rare) and their vinylic side chains resist hydrogenation. Again, the u.v. spectra are those of simpler quinones and give no indication of extended conjugation. Evidently the propenyl group is rotated out of plane in order to avoid collisions with the adjacent methyl group and oxygen atom, which then protect both sides of the vinylic bond from the approach of reagents. In order to place the structure of quinone (**7**) beyond doubt we attempted an alternative synthesis and found this difficult to achieve. For example, the ketone (**9**) failed to react with methylenic Wittig reagents, presumably because of steric hindrance, and the iodoquinone (**10**) failed to react with vinylic or other cuprates, presumably because the quinone oxidises such reagents. Eventually, 2-isopropyl-3-methyl-1,4-naphthoquinone (**11**) with *N*-bromosuccinimide (NBS) gave the bromomethylquinone (**12**) which, in flash vacuum pyrolysis,[5] furnished the required compound (**7**) though only in very low yield. The reaction requires an elimination to provide a double quinonemethide (**13**) and a sigmatropic shift of hydrogen within this.



(**9**)

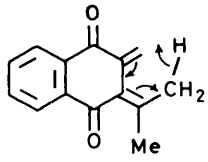


(**10**)



(**11**) R = H

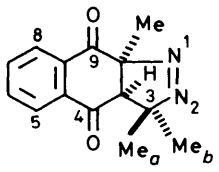
(**12**) R = Br



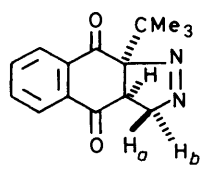
(**13**)

The adduct (**1**) was also treated with potassium hydroxide at reduced concentrations, originally with the intent of obtaining the monoquinone (**7**) while avoiding the subsequent change into the diquinone (**6a**). In practice the reaction is much slower and appears to allow time for the initial carbanion (**4**) to react with oxygen (if air is not excluded) because the main product is now the colourless quinone epoxide (**14**) formed, we suggest, as indicated in Scheme 2. The structure of the epoxide is established by the ^{1}H n.m.r. spectrum, which defines the nature of the alkyl groups, the i.r. spectrum, which exhibits bands appropriate to acetophenone-type carbonyl groups but none for hydroxy groups, and the electronic spectrum, which is again that of an acetophenone chromophore, devoid of bands in the visible region.

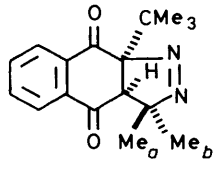
As stated at the outset, the reaction between methyl-1,4-naphthoquinone and 2-diazopropane at low temperatures affords an additional product to which structure (**15**) has been assigned. The same compound is obtained by treating adduct (**1**) with further diazopropane at −50 °C; remarkably, even lower temperatures do not prevent this seemingly very hindered reaction. We wondered whether some adventitious catalyst might be responsible but redoubled efforts to remove protic substances from the diazopropane had no effect, nor did the addition of traces of likely impurities such as water, mercury, mercury chlorides, and hydrazine.



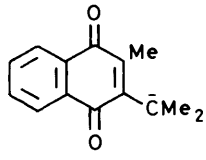
(**1**)



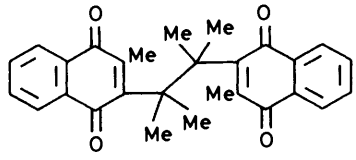
(**2**)



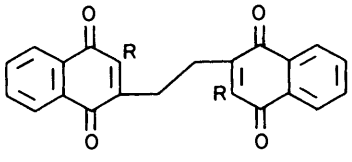
(**3**)

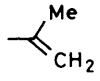


(**4**)

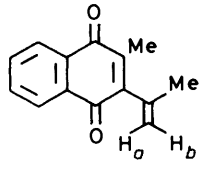


(**5**)

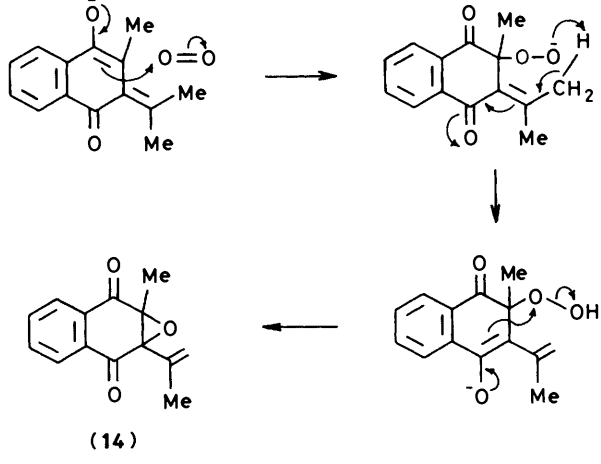


(**6a**) R = 

(**6b**) R = $CHMe_2$



(**7**)



(**14**)

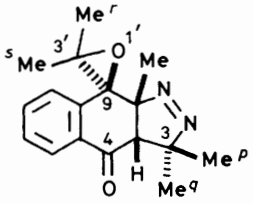
Scheme 2.

Standard chemical spectroscopic methods did not suffice to determine the spiran structure completely. Chemically, the compound is much more stable than simple analogies suggest. Unlike any other quinone–diazoalkane adduct known to us, compound (**15**) not only gives a (low intensity) molecular ion at 284 a.m.u., but also a fragment ion at 269 a.m.u. that clearly

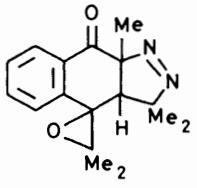
Table 2. ^{1}H N.m.r. spectra of derivatives of 1,4-naphthoquinone[a]

Compd.	Assignments: 2-Me	$CHMe_2$	$CHMe_2$	5-, 8-H	6-,7-H	CH_2	$=CH_2$	Vinylic Me
(6a)				8.08	7.75	2.86	4.90, 5.37	1.89
(6b)		1.44	3.38	8.06	7.69	2.83		
(7)	2.17			8.07	7.70		4.88, 5.37	2.00
(10)	2.48			8.11	7.72			
(11)	2.03	1.38	3.27	8.03	7.75			
(12)		1.44	3.25	8.07	7.71	4.54		
(14)	1.61			7.98	7.73		5.23, 5.36	1.95

[a] At 220 MHz in $CDCl_3$ with tetramethylsilane as internal reference; δ scale. All relative intensities are appropriate to the assignments. All aromatic bands consisted of overlapping multiplets and were not analysed.



(15)



(16)

corresponds to the loss of a methyl group *before* the loss of nitrogen. The oxirane (**15**) is hardly affected by methanolic potassium hydroxide or by cold ethanolic hydrogen chloride, and refluxing acid caused only slow complex decomposition during 4 h. Thus we were left without a chemical means of determining whether the oxirane system had been formed at position 9 giving product (**15**), as assumed so far, or at position 4 giving compound (**16**). The common spectroscopic methods also failed to solve this problem as well as remaining ambiguous as to the stereochemistry at the spiro atom. These problems were eventually solved by the use of selective Overhauser enhancements disclosed by difference spectroscopy,[6] as already reported briefly.[7]

The details of the high-field ^{1}H and ^{13}C n.m.r. spectra are listed in Tables 3 and 4 The signals from the methine group at position 3a can be recognised immediately and unambiguously on the basis of shift and multiplicity, the carbon resonating at δ_C 60.94 and the proton at δ_H 2.37. The carbonyl carbon resonates at δ_C 195.0; two signals close to δ_C 90 belong to atoms not attached to hydrogen and have to be assigned to carbon attached to the azo link. Single-frequency pre-irradiation at δ_H 2.37 produces an n.O.e. of all these three carbon signals, proving that the methine group is approximately the same distance from all of them. This is possible only if the carbonyl group is at position 4 as in structure (**15**).

Although there are numerous couplings over various distances (Tables 3 and 4) they do not lead to unequivocal assignments, whereas n.O.e. measurements lead to a unique spatial connectivity for the protons. The chain begins with the proton at position 5 recognised by its low-field shift and the fact that it is adjacent to one other proton only, that at position 6. The chain passes *via* position 7 to the proton at position 8 which is found to interact with the protons of one methyl group that can only be Me^s of the oxirane residue. The chain continues to

Table 3. ^{1}H N.m.r. spectral parameters for spiran (**15**) in $CDCl_3$ at 400 MHz

Proton	Chemical shift (δ scale)	Coupling constant (Hz)
3-Me^p	1.833	
3-Me^q	1.217	
3a-H	2.370	
5-H	7.878	$J_{5,6}$ 7.7, $J_{5,7}$ 1.5, $J_{5,8}$ 0.5
6-H	7.460	$J_{5,6}$ 7.7, $J_{6,7}$ 7.0, $J_{6,8}$ 1.3
7-H	7.643	$J_{6,7}$ 7.0, $J_{7,8}$ 7.7, $J_{5,7}$ 1.5
8-H	7.552	$J_{7,8}$ 7.7, $J_{6,8}$ 1.3, $J_{5,8}$ 0.5
9a-Me	1.659	
3'-Me^r	1.536	$J_{3'a,3'b}$ 0.5
3'-Me^s	0.962	$J_{3'a,3'b}$ 0.5

p cis to 9a-Me; *q trans* to 9a-Me; *r syn* to C-9a; *s anti* to C-9a.

Table 4. ^{13}C N.m.r. spectral parameters for spiran (**15**) in $CDCl_3$ at 100 MHz

Carbon	Chemical shift (δ scale)	Coupling constant (Hz) to ^{1}H
C-3	90.00	$J_{C\text{-}3,H\text{-}3a} = J_{C\text{-}3,Me^p} = J_{C\text{-}3,Me^q} = 5$
C-3a	60.94	$J_{C\text{-}3a,3a\text{-}H}$ 128
C-4	194.98	$J_{C\text{-}4,3a\text{-}H} = J_{C\text{-}4,5\text{-}H}$ 4
C-4a	134.66	$J_{C\text{-}4a,6\text{-}H} = J_{4a,8}$ 7
C-5	126.50	$J_{C\text{-}5,5\text{-}H}$ 164, $J_{C\text{-}5,7\text{-}H}$ 8
C-6	128.41	$J_{C\text{-}6,6\text{-}H}$ 166, $J_{C\text{-}6,8\text{-}H}$ 8
C-7	133.46	$J_{C\text{-}7,7\text{-}H}$ 164, $J_{C\text{-}7,5\text{-}H}$ 8
C-8	128.19	$J_{C\text{-}8,8\text{-}H}$ 166, $J_{C\text{-}8,6\text{-}H}$ 8
C-8a	140.23	$J_{C\text{-}8a,5\text{-}H} = J_{C\text{-}8a,7\text{-}H} = 7$
C-9	69.42	$J_{C\text{-}9,9a\text{-}Me} = J_{C\text{-}9,Me^r} = J_{C\text{-}9,Me^s} = 5$
C-9a	90.45	$J_{C\text{-}9a,Ca\text{-}H} = J_{C\text{-}9a,Me^r} = 5$
$3CH_3{}^p$	28.72	$J_{CH_3{}^p,CH_3{}^p}$ 130
$3\text{-}CH_3{}^p$	20.60	$J_{CH_3{}^p,3a\text{-}H} = J_{CH_3{}^p,CH_3{}^p} = 5$ $J_{CH_3{}^q,CH_3{}^p}$ 133
$9a\text{-}CH_3$	24.91	$J_{CH_3{}^q,3a\text{-}H} = J_{CH_3{}^q,CH_3{}^p} = 5$ J_{CH_3,CH_3} 129 $J_{CH_3,3a\text{-}H}$ 7
C-3'	68.77	Unresolved multiplet
$3'\text{-}CH_3{}^r$	25.05	$J_{CH_3{}^r,CH_3{}^r}$ 128 $J_{CH_3{}^r,CH_3{}^s}$ 3
$3'\text{-}CH_3{}^s$	20.98	$J_{CH_3{}^r,CH_3{}^r}$ 130 $J_{CH_3{}^r,CH_3{}^s}$ 5

p trans to 9a-Me; *q cis* to 9a-Me; *r syn* to C-9a; *s anti* to C-9a.

the other oxirane methyl group (Me^r) and then, rather surprisingly, to the methyl group Me^q at position 3. From here connectivity links Me^q with the other methyl group (Me^p) at position 3 and this with the methine proton at position 3a. The methyl resonance at δ_H 1.66 shows n.O.e. only with respect to the methine proton and cannot be ascribed to any group other than that at position 9a which is the terminus of the sequence. The complete sequence with assignments is as follows:

5-H	6-H	7-H	8-H	3'-Me^s
δ 7.88	7.46	7.64	7.55	0.96
				|
9a-Me	3a-H	3-Me^p	3-Me^q	3'-Me^r
δ 1.66	2.37	1.84	1.22	1.54

Two n.O.e. effects are of particular significance. That between the methyl group at position 9a and the proton at position 3a

proves that the ring fusion is *cis*; that between the oxirane methyl group Me^r and the pyrazoline Me^q at position 3 establishes the relative stereochemistry of the oxirane ring and also the conformation of the flexible part of the system which must bring these groups close together. When the conformation is correctly arranged, models show that Me^s is somewhat shielded by the benzene ring, and Me^q by the carbonyl group; the other methyl groups are not so shielded and afford signals at lower field.

Models suggest that the spiran (**15**) is the least crowded of the four isomers that might have been formed, which may explain the regiospecificity of the reaction, but they also show that any approach of 2-diazopropane to the adduct (**1**) will be hindered so that the relative speed of the reaction at lower temperatures seems unusual. In order to produce spiran (**15**) the diazoalkane orbitals are for a time adjacent to those of the pyrazoline azo link and there may be favourable secondary orbital interactions between them. A few allied situations have been described.[8]

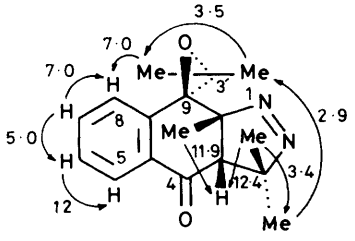


Figure 1. The chief nuclear Overhauser enhancements (%) from the ^{1}H-{^{1}H} n.m.r. spectra of the dihydrobenzindazole (**15**) in $CDCl_3$

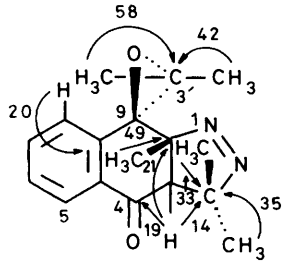


Figure 2. The nuclear Overhauser enhancements (%) from the ^{1}H-{^{1}C} n.m.r. spectra of dihydrobenzindazole (**15**) in $CDCl_3$

Experimental

U.v. spectra were recorded using a Pye-Unicam SP8-100 spectrophotometer. Solutions were 10^{-4}M in 95% ethanol, with ultrasound to effect solution. I.r. spectra were obtained from KBr discs by means of a Perkin-Elmer 125 spectrophotometer. M.p.s were obtained using a hot-stage microscope and are uncorrected. Mass spectra were obtained using an AEI MS-12 instrument.

^{1}H N.m.r. spectra were obtained at 220 MHz in $CDCl_3$ with $SiMe_4$ as internal reference using a Perkin-Elmer R34 n.m.r. spectrometer. All 400 MHz ^{1}H and 100 MHz ^{13}C n.m.r. spectra were obtained using a Bruker WH-400 n.m.r. spectrometer and the results are given in Tables 1 and 2 and in Figures 1 and 2.

Diethyl ether (ether) was dried by distillation from sodium and benzophenone. Light petroleum refers to that fraction boiling in the range 60—80 °C and was distilled before use.

(3aRS,9aSR)-3a,9a-*Dihydro*-3,3,9a-*trimethylbenz*[f]*indazole*-4,9-(3H)-*dione* (**1**).—A very gently stirred solution of 2-methyl-1,4-naphthoquinone (8.6 g, 0.05 mol) in ether (500 ml) was cooled to 0 °C and ethereal 2-diazopropane[9] [from acetone hydrazone (3.6 g, 0.05 mol)] was added. The red colour of the diazoalkane was instantly discharged and 12 h later removal of solvent provided a brown solid. Column chromatography on silica with light petroleum–ether mixtures as eluants first gave 2-methyl-1,4-naphthoquinone (5.4 g recovery) followed by the title *dihydroindazoledione* (2.38 g, 53% based upon consumed quinone), which crystallised from light petroleum as off-white rods, m.p. 102—105 °C (decomp.); $\lambda_{min.}$ 229, 255, 302, and 311 nm (log ε 4.49, 4.05, 3.27, and 3.25); $\nu_{max.}$(KBr) 3 340 (overtone of extremely strong band at 1 672), 2 970—2 860, 1 672vs, 1 582, and 1 552 cm^{-1} (N=N); *m/z* 214 (52) ($M - N_2$, implying *M* 242), 199 (14), 185 (18), 184 (16), 170 (28), 142 (18), 140 (13), 127 (31), 114 (36), and 104 (100%) (Found: C, 69.0; H, 5.6; N, 11.3. $C_{14}H_{14}N_2O_2$ requires C, 69.12; H, 5.79; N, 11.57%).

The dihydroindazoledione was formed in better yield (60%) when 2-diazopropane (from 5 equiv. of acetone hydrazone) was added to an ether solution of 2-methyl-1,4-naphthoquinone (1 equiv.) at −45 °C, under which conditions it separated as a dense white precipitate and was isolated by filtration without allowing the mixture to warm up.

(3aRS,9RS,9aSR)-3a,9a-*Dihydro*-3,3,3′,3′,9a-*pentamethylspiro*[9H-*benz*[f]*indazole*-9,2′-*oxirane*]-4-(3H)-*one* (**15**).—(i) A very gently stirred solution of 2-methyl-1,4-naphthoquinone (1.72 g, 0.01 mol) in ether (100 ml) at −78 °C was treated with ethereal 2-diazopropane [from acetone hydrazone (3.6 g, 0.05 mol)]. The red colour of the diazoalkane was rapidly discharged and the solution turned dark brown after 2 min. After several hours at −78 °C the solution was allowed to warm to room temperature and the solvent was removed to leave a brown solid, whose n.m.r. spectrum indicated a mixture of two products. Separation was achieved using medium-pressure column chromatography through a 1 m × 4 cm diameter column of silica (Fluka GF254) with pentane, then light petroleum–ether mixtures as eluants. The dihydroindazoledione (**1**) was obtained first, then a new product that separated from light petroleum to give a *spiran* (**15**) as white rhombs (0.35 g, 12%), m.p. 168—170 °C (decomp.); $\lambda_{max.}$ 212, 254, 292, and 333 nm (log ε 4.29, 3.96, 3.20, and 2.54); $\nu_{max.}$(KBr) 3 060, 2 980—2 850, 1 725, 1 670, 1 592, and 770 cm^{-1}; *m/z* 284 (M^+, 0.13), 269 (6), 256 (12), 241 (15), 228 (7), 215 (14), 213 (16), 199 (8), 198 (11), 197 (14), 184 (44), 155 (100), 141 (26), 128 (46), and 105 (49%) (Found: C, 71.6; H, 7.1; N, 9.8. $C_{17}H_{20}N_2O_2$ requires C, 71.80; H, 7.09; N, 9.85%).

(ii) The dihydroindazoledione (**1**) (100 mg) was dissolved in ether (20 ml) containing just enough dichloromethane to effect solution. The solution was cooled to −50 °C and an excess of 2-diazopropane was added until the red colour of the diazoalkane persisted even after warming to room temperature. After 12 h, removal of solvent and column chromatography on silica with light petroleum–ether mixtures gave the spiran (**15**) (60 mg).

(3aRS,9aSR)-3a,9a-*Dihydro*-9a-*t-butylbenz*[f]*indazole*-4,9(3aH)-*dione* (**2**).—2-t-Butyl-1,4-naphthoquinone[10] (1 g) was treated in ether (300 ml) at 0 °C with dry (KOH) diazomethane [from Diazald (16 g)] in ether; after 18 h removal of the solvent left a solid contaminated by a trace of yellow oil. Recrystallisation of the solid from light petroleum (charcoal) gave the *dihydroindazole* (**2**) as matted needles (0.85 g, 63%), m.p. 108—111 °C (decomp.); $\lambda_{max.}$ 227, 251sh, and 302 nm (log ε 4.50, 4.04, and 3.26); $\nu_{max.}$ 1 705sh, 1 698, 1 677, and 1 594 cm^{-1}; *m/z* 256 (M^+, 0.3), 228 (4), 213 (6), 195 (6), 185 (14), 173 (19), 172 (100), and 104 (54%) (Found: C, 70.4; H, 6.6; N, 10.9. $C_{15}H_{16}N_2O_3$ requires C, 70.3; H, 6.3; N, 10.9%).

(3aRS,9aSR)-3a,9a-*Dihydro*-3,3-*dimethyl*-9a-*t-butylbenz*[f]-*indazole*-4,9(3H)-*dione* (**3**).—A solution of 2-t-butyl-1,4-naph-

thoquinone (0.4 g) in ether (300 ml) at 0 °C was treated with diazopropane prepared from acetone hydrazone (0.4 g) and mercury(II) oxide. Next day, evaporation of the solvent and chromatography of the residue on silica with ether–light petroleum gave first the starting quinone (0.2 g) then the *dihydroindazoledione* (**3**) which separated from ether–light petroleum (charcoal) as irregular needles (50 mg), m.p. 133—135 °C (decomp.); $\lambda_{max.}$ 229, 254, 299, and 307sh nm (log ε 4.43, 3.93, 3.16, and 3.15); $\nu_{max.}$ 1 675vs, 1 590, and 1 555w cm^{-1}; *m/z* 285 (*M* + 1), 284 (M^+, 0.1), 257 (0.4), 256 (0.4), 241 (1), 213 (1), 201 (14), and 200 (100%) (Found: C, 71.7; H, 7.1; N, 9.95. $C_{17}H_{20}N_2O_2$ requires C, 71.8; H, 7.1; N, 9.85%).

Reactions between the Dihydroindazoledione (**1**) *and Potassium Hydroxide in Methanol.*—(i) *With* 0.25M *base.* A solution of the dione (**1**) (0.2 g) in methanol (3 ml) was mixed with M-potassium hydroxide in methanol (1 ml) at 18 °C. There was a brisk evolution of nitrogen and the mixture became deep red; a yellow precipitate was deposited after a short time and was collected and washed thoroughly with methanol. This product appeared from t.l.c. and spectroscopy to be an analytically pure single compound, and since its solubility relations were unsatisfactory in all the solvents tried it was dried at 80 °C at 0.01 mmHg to give *3,3′-di-isopropenyl-2,2′-ethylenedi-1,4-naphthoquinone* (**6a**) as yellow rhombs (0.12 g, 69%), m.p. 225—229 °C; $\lambda_{max.}$ 249, 257sh, and 332 nm (log ε 4.57, 4.47, and 3.76); $\nu_{max.}$ 1 687w, 1 660br, 1 600, and 1 584 cm^{-1}; *m/z* 426 (*M* + 4, 3), 424 (*M* + 2, 7), 422 (*M*, 3), 213 (33), 212 (100), 211 (80), 197 (47), and 115 (60%) (Found: C, 79.3; H, 5.4. $C_{28}H_{22}O_4$ requires C, 79.6; H, 5.2%).

(ii) *With quenching.* A solution of the dione (**1**) (0.2 g) in a mixture of dichloromethane (1 ml) and methanol (5 ml) was treated with methanolic potassium hydroxide as in (i), but 1 min after the addition and before any precipitate appeared the reaction was quenched with acetic anhydride (25 ml) added all at once. The solution added to water (120 ml) and when the anhydride had been destroyed the mixture was neutralised with solid sodium carbonate. The product was collected into ether (3 × 100 ml), the extract was dried ($MgSO_4$), and the product was recovered in the usual way. Crystallisation of the residue (0.115 g) from wet methanol gave *2-isopropenyl-3-methyl-1,4-naphthoquinone* (**7**) as yellow needles (60 mg), m.p. 76—79 °C; $\lambda_{max.}$ 245sh, 251, 259, and 329 nm (log ε 4.26, 4.28, 4.22, and 3.41); $\nu_{max.}$ 1 685vs and 1 587 cm^{-1}; *m/z* 212 (M^+, 100), 211 (19), 197 (57), 115 (48), 105 (57), and 104 (71) (Found: C, 79.05; H, 5.8. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%).

(iii) *With dil. base.* The dione (**1**) (1.22 g) was dissolved in the minimum volume of dichloromethane and the solution was diluted with methanol to 50 ml. M-Methanolic potassium hydroxide (5.2 ml) was added drop by drop and air was blow in very gently. After 70 min the initially red solution had turned yellow; it was concentrated, diluted with ether (50 ml), kept at −5 °C overnight, and then filtered. The solution was washed with water (2 × 100 ml), dried ($MgSO_4$), and left to evaporate, to afford a brown solid (0.81 g), which was crystallised from wet ethanol to give *2-isopropenyl-3-methyl-1,4-naphthoquinone 2,3-epoxide* (**14**) as rods, m.p. 84—85 °C; $\lambda_{max.}$ 230, 303, and 337 nm (log ε 4.44, 3.30, and 2.47); $\nu_{max.}$ 1 695 and 1 590 cm^{-1}; *m/z* 228 (M^+, 6), 213 (8), 199 (64), 187 (68), 186 (100), 171 (35), 159 (38), 157 (50), 131 (73), 129 (71), and 128 (85%) (Found: C, 73.5; H, 5.4. $C_{14}H_{12}O_3$ requires C, 73.7; H, 5.3%).

2-Iodo-3-methyl-1,4-naphthoquinone (**10**).—1,4-Dimethoxy-2-methylnaphthalene (15.2 g) was dissolved in tetrachloromethane (500 ml) and powdered potassium carbonate (50 g) was added. To the stirred mixture at −8 °C was added a solution of bromine (3.9 ml) in tetrachloromethane (200 ml), gradually during *ca.* 4 h. The mixture was left overnight, then filtered through Celite, and the residue was washed with ether. The filtrate and washings were combined and the solvents removed under reduced pressure; the remanent solid was crystallised from hexane–benzene to give 2-bromo-1,4-dimethoxy-3-methylnaphthalene[11] (93%), m.p. 72—74 °C (lit., 84—85 °C).

This compound (2.8 g) was dissolved in freshly dried (sodium–benzophenone) tetrahydrofuran (150 ml) and the solution was stirred under nitrogen at −20 °C while butyl-lithium (1.43M) in pentane (14 ml) was added (lower temperatures allow the solute to crystallise), and after 2 min the solution was cooled to −78 °C and stirred for a further 30 min to permit a precipitate to form. Then a solution of iodine (5 g) in ether was added until the colour persisted, and the mixture was allowed to regain room temperature. The usual washing with aqueous sodium thiosulphate, drying ($MgSO_4$), and removal of solvents left a solid that crystallised from aqueous methanol to afford *2-iodo-1,4-dimethoxy-3-methylnaphthalene* as plates (2.6 g, 79%), m.p. 68—73 °C (decomp.) (Found: M^+, 327.995. $C_{13}H_{13}IO_2$ requires *M*, 327.996).

A solution of the iodo compound (5 g) in dichloromethane (50 ml) was treated at −80 °C with a solution of boron tribromide (4 ml) in dichloromethane (20 ml) for 2 h, then left to regain room temperature. Air was not excluded, and the solution became black; when filtered through deactivated alumina (5% water) the mixture gave a clear yellow solution which, on work-up, gave the *iodoquinone* (**10**) as dark yellow plates (2.41 g, 52%), m.p. 152—155 °C (subl. >115°C) (from trichloromethane–light petroleum) (Found: M^+, 297.946. $C_{11}H_7IO_2$ requires *M*, 297.949).

Preparation and Flash Vacuum Pyrolysis of Compound (**12**).—2-Isopropyl-3-methyl-1,4-naphthoquinone[4] (1 g) in refluxing tetrachloromethane (45 ml) was allowed to react with NBS (1.5 g) and catalytic amounts of dibenzoyl peroxide. Spectroscopy indicated that conversion was better than 98%, but when the solvents were removed the intensely yellow solid that remained deteriorated when attempts were made to purify it by conventional means and it was, therefore, not subjected to elementary analysis but was characterised as 2-bromomethyl-3-isopropyl-1,4-naphthoquinone (12) by ^1H n.m.r. spectroscopy (Table 2) and the mass spectrum, *m/z* 292/4 (6), 251/3 (2), 214 (53), 213 (100), 199 (20), 198 (18), 197 (20), 185 (24), 171 (32, 157 (23), 141 (26), 122 (80), 115 (52), and 105 (80%).

The bromomethylnaphthoquinone (0.12 g) was pyrolysed at 600 °C/0.08 mmHg with nitrogen as carrier gas in a silica reaction tube (length 20 cm) with no packing.[5] The pyrolysate was collected at a cold finger (solid CO_2 in propan-2-ol) and the crude vinylic quinone (15 mg, 12%) was identified after chromatography on silica with light petroleum as eluant. Pyrolysis conditions were varied but better yields were not secured.

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