# Thermal Decomposition of Homoquinones

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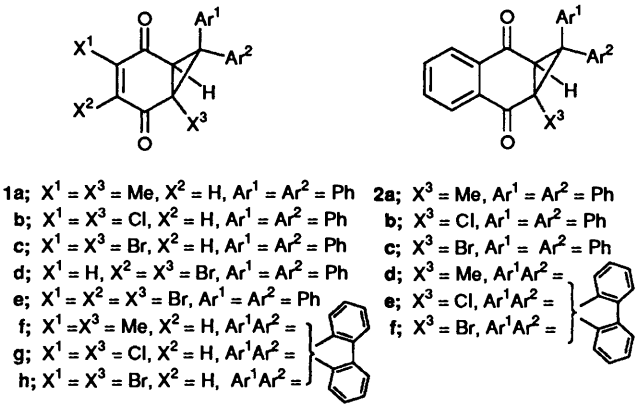
Thermolysis of diphenyl- and biphenyl-2,2'-diyl-substituted homobenzoquinones **1** and homonaphthoquinones **2** with substituents $X^3$ (= Me, Cl, Br) has been investigated at 100 °C. The biphenyl-2,2'-diylhomoquinones **1** and **2** bearing halogeno substituents were thermolysed to 2-(9-halogenofluoren-9-yl)-1,4-benzoquinones **8g, h** and -1,4-naphthoquinones **19e, f**, respectively, *via* a cyclopropane ring-opening reaction. The diphenylhomoquinones were thermally less labile so that only ones bearing a bromo substituent underwent a cyclopropane ring-opening to afford a different type of product, 2-bromo-3-diphenylmethylene-2,3-dihydro-1,4-benzoquinones **3c–e** and -1,4-naphthoquinone **10**, respectively. The product change was attributed to the steric requirement of the intermediary allyl cations. On further heating, compounds **3c–e** were converted into xanthylium salts *via* a 6π electrocyclization, whereas compound **10** was transformed into the coupling dimer *via* an allyl radical. The different behaviour of the bromo quinones **3c–e** and **10** was interpreted on the basis of Frontier Molecular Orbital considerations.

Fusion of a functional component to a cyclopropane ring is expected to endow new structural and electronic features to a useful synthetic intermediate, because cyclopropane derivatives undergo a variety of ring-cleavage reactions.[1] Thermolysis of cyclopropanes with labile leaving groups like halogens,[2] tosyl[3] and diazonium ion[4] are well known to give propenes through a concerted process, with ring-opening occurring simultaneously with departure of the leaving group. The thermal rearrangement of cyclopropanes is the subject of considerable mechanistic attention, since the orbital correlation diagram criteria predict the stereospecific and disrotatory motion in the sense of cyclopropyl–allyl cation transformation.[5]

Recently, we have prepared quinone-fused cyclopropanes, so-called homoquinones, in the dipolar addition of diaryldiazomethanes to variously substituted quinones.[6] In view of the electrophilic and conjugative properties of quinones, it is of interest to obtain insight into the physicochemical properties due to the strained bicyclic systems and to shed light on their potential utility as synthetic candidates. However, there are only a few scattered studies concerning the skeletal transformation and the synthetic uses of these ring-condensed systems.[7]

This paper deals with the thermolysis of diphenyl- and biphenyl-2,2'-diyl-substituted homobenzoquinones **1** and homonaphthoquinones **2**,[8] with substituents $X^3$ (= Me, Cl, Br). The aim of this study is to explore the basic structural and mechanistic features of thermal reactions of these homoquinones.




## Results and Discussion

*Thermolysis of Diphenylhomobenzoquinones* **1a–e**.—A solution of bromo-substituted diphenylhomobenzoquinone **1c** in benzene was heated in a sealed glass tube at 100 °C for 2 days to give, almost quantitatively, clear reddish orange crystals (Table 1, entry 3). The absorption spectrum recorded in acetonitrile was characterized by several strong absorptions with $\lambda_{max}$ 227 nm (log ε 4.40), 249 (436), 270 (4.42), 408 (4.53) and 491 (3.82).†[9] Similarly, thermolysis of bromo-substituted compounds **1d** and **1e** occurred to furnish reddish precipitates in excellent yields (entries 6 and 7). These crystals did not melt; instead they decomposed at 250–340 °C and were found to have the same molecular formulae as the homobenzoquinones. The IR spectra revealed no carbonyl absorption, but typical broad bands in the range of 2600–3050 $cm^{-1}$, indicating the aromatization of the quinone framework. It was also noted that the addition of excess of perchloric acid brought about an anion-exchange reaction to yield analogous red crystals containing the perchlorate ion.

These chemical and spectral observations offer hard evidence for these salt-like pyrolysates to be xanthylium ions **4c–e** (Scheme 1). A confirmatory indication for xanthylium salts was also provided by the formation of xanthene derivative **5c** when treated with diazomethane in methanol. Thus, the introduction of a methoxy group at the C-9 position of compound **5c** is due to the nucleophilic attack of methanol, because the behaviour of the xanthylium ion is best thought of in terms of its resonance form, that is, the carbenium ion with positive charge at the C-9 position.[10]

Xanthene derivative **5c** can be converted into the xanthylium salt **6c** by addition of a slight excess of strong acid (HXs) such as perchloric, sulfuric, nitric, hydrochloric, hydrobromic, or even trifluoroacetic acid, as indicated by the sudden colouration to reddish orange.

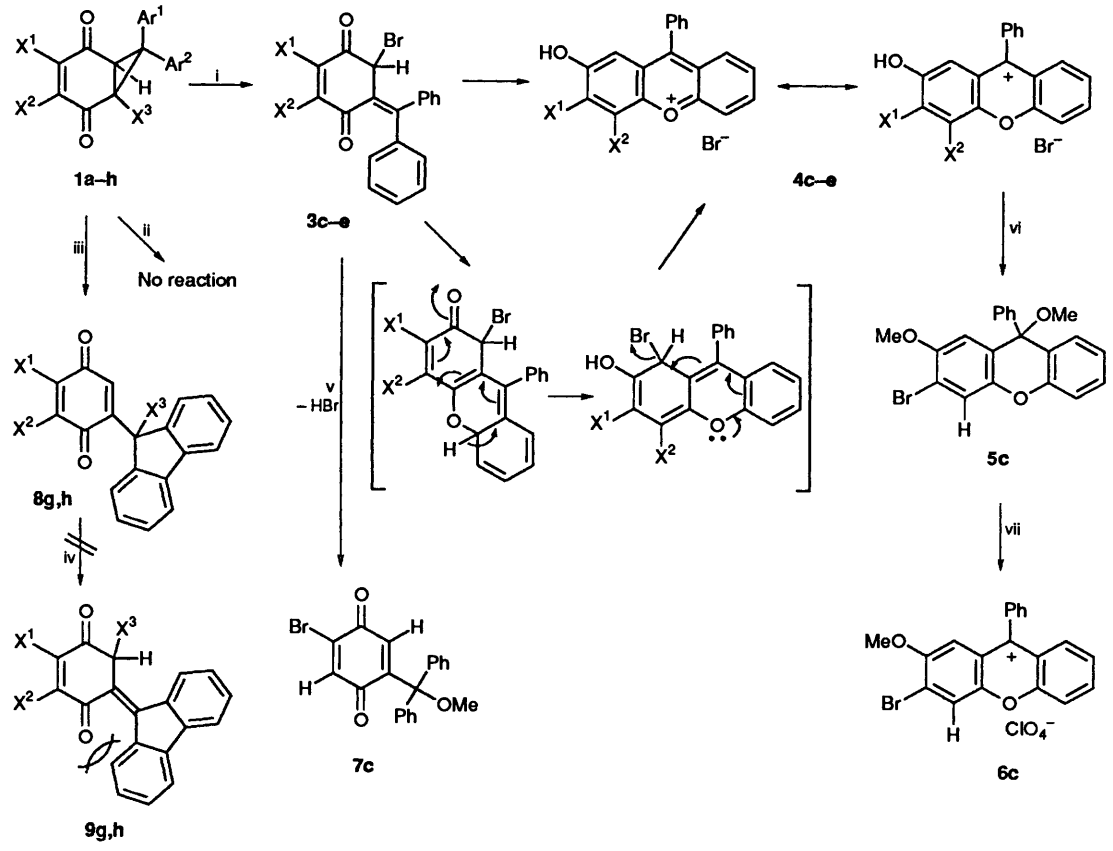
Formation of xanthylium salts suggests the participation of the ring-opened 2-bromo-3-diphenylmethylene-2,3-dihydro-

† The absorption pattern is very similar to that of 9-phenylxanthylium.[9]

**Table 1** Thermolysis of homobenzoquinones **1a–h** at 100 °C in benzene[a]

| Entry | Cyclopropane | Reaction time (*t*/day) | Yield (%)[b] 3 | 4 | 7 | 8 |
|---|---|---|---|---|---|---|
| 1 | **1a** | 5 | | No reaction | | |
| 2 | **1b** | 5 | | No reaction | | |
| 3 | **1c** | 2 | trace | 97 (96)[c] | 0 | |
| 4 | **1c**[d] | 1 | 0 | 0 | 89 | |
| 5 | **1d** | 1 | 35 | 58 | | |
| 6 | **1d** | 3 | trace | 95 | | |
| 7 | **1e** | 3 | trace | 96 | | |
| 8 | **1f** | 7 | | No reaction | | |
| 9 | **1g** | 0.1 | | | | 100 |
| 10 | **1h**[e] | | | | | 100 |

[a] Thermolysis was made on 4–5 × $10^{-1}$ mol $dm^{-3}$ solutions. [b] Isolated yields. [c] Value in parenthesis was obtained in solvent toluene. [d] Reaction was carried out in the presence of methanol (20% by volume). [e] Spontaneously decomposed at room temperature.



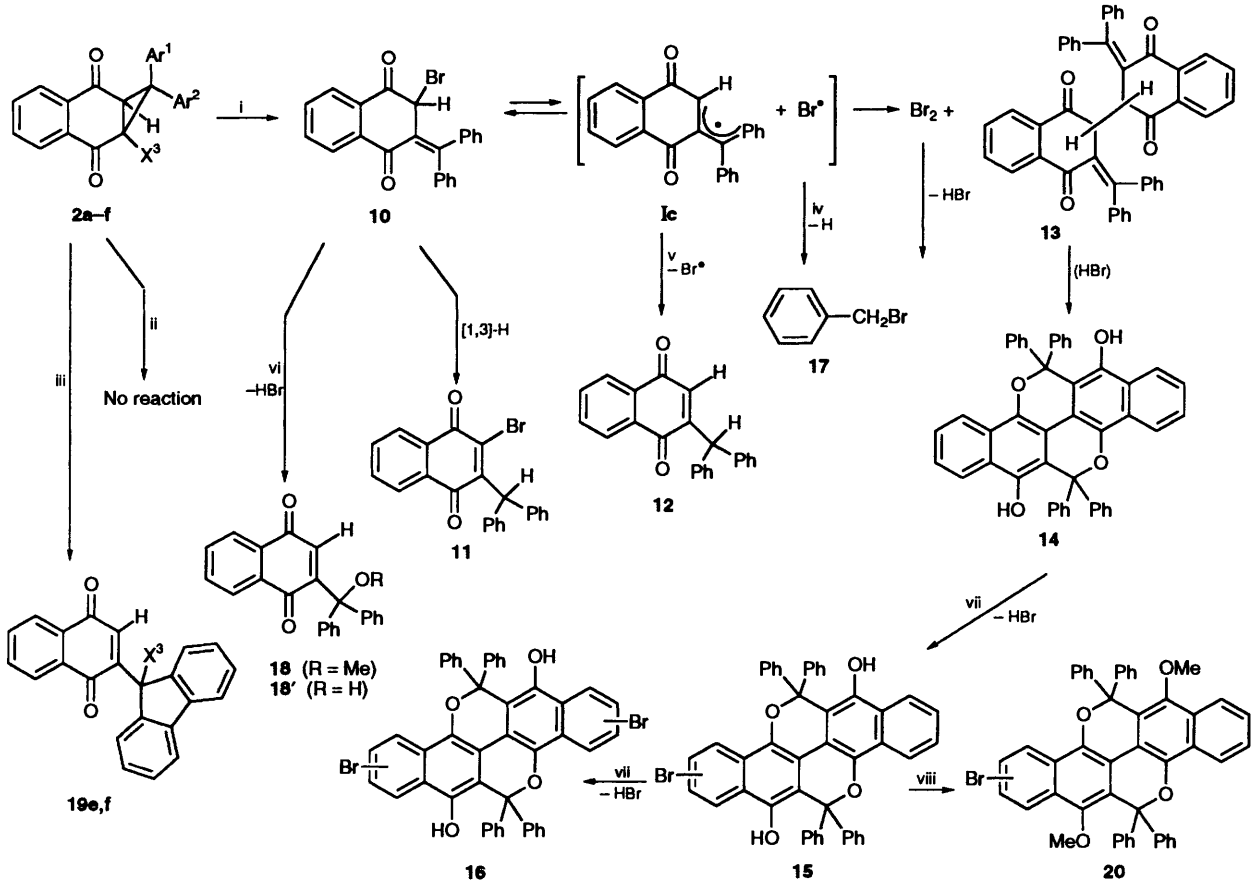

**Scheme 1** *Reagents and conditions:* i, **1c–e**, 100 °C; ii, **1a**, **b**, **f**, 100 °C; iii, **1g**, **h**, room temp.–100 °C; iv, 100 °C; v, MeOH; vi, $CH_2N_2$, MeOH; vii, $HClO_4$

1,4-benzoquinones **3c–e** as key intermediates. In fact, thermolysis of compound **1c** in the presence of additive methanol (20% by volume) gave rise to the captured 2-bromo-5-[(methoxy)(diphenyl)methyl]-1,4-benzoquinone **7c** (89%) instead of the xanthylium salt (entry 4). Furthermore, we succeeded in isolating such an intermediate **3d** for the case of dibromide **1d** (entry 5), and confirmed its transformation into the corresponding xanthylium salts **4d** on further heating.

Mechanistically, it can be seen in Scheme 1 that thermolysis of bromo-substituted homobenzoquinones **1c–e** proceeds through a reaction sequence involving an initial cleavage of the cyclopropane ring to give compounds **3c–e**, followed by a 6π electrocyclization, and an electron reorganization associated with proton migration and the release of $Br^-$. Similar thermal electrocyclization of a dienone structure was reported for valence isomerization of *cis*-β-ionone to 2*H*-pyran.[11]

In contrast to the bromo-substituted homobenzoquinones, the corresponding methyl- and chloro-substituted homologues **1a** and **1b** were recovered unchanged even after being heated for 5 days under the same conditions.

*Thermolysis of Biphenyl-2,2′-diylhomobenzoquinones* **1f–h**.— We attempted to obtain biphenyl-2,2′-diylhomobenzoquinones from the reaction of 9-diazofluorene (9-DF) with the corresponding 1,4-benzoquinones. The methyl- and the chloro-substituted quinones provided desired homobenzoquinones, **1f** and **1g**, but the bromo-substituted quinone produced spontaneously ring-opened 2-(9-bromofluoren-9-yl)-1,4-benzoquinone **8h** in quantitative yield (entry 10). This direct degradation means that bromo-substituted biphenyl-2,2′-diylhomobenzoquinone **1h** is thermally labile owing to the favourable bisected conformation for π-conjugation.[12] Namely,




**Scheme 2** *Reagents and conditions:* i, **2c**, 100 °C; ii, **2a**, **b**, **d**, 100 °C; iii, **2e**, **d**, room temp.–100 °C; iv, toluene; v, HBr; vi, ROH; vii, $Br_2$; viii, $CH_2N_2$, benzene

the planar biphenyl-2,2′-diyl group is capable of providing a π-electron to the breaking cyclopropane bond to a better extent than can the twisted diphenyl group. Thus, heating of chloro-substituted substrate **1g** readily brought about ring-cleavage to furnish compound **8g** (entry 9), though the methyl-substituted analogue **1f** remained unchanged after 1 week's heating at 100 °C (entry 8).

The ring-opening facility of the present homobenzoquinones decreases in the order of **1h** > **1g** > **1c–e** > **1a**, **b**, **f**; *i.e.*, $X^3$ = Br > Cl > Me and biphenyl-2,2′-diyl > diphenyl. The relative ease for halogeno substituents is not surprising since it follows the order of reactivity (Br > Cl) observed for other ring-condensed halogenated cyclopropanes; 7,7-dihalogenobicyclo[4.1.0]heptanes,[13] and 3,3-dihalogenotricyclo[3.2.1.$0^{3,4}$]octanes.[14]

*Structural Effects of Diaryl Groups.*—According to the generally accepted mechanism,[5] thermolysis of the present homobenzoquinones is likewise thought to occur by way of concerted ring-opening followed by the recombination of halide with the resulting quinone-fused allyl cations **Ia** and **Ib** (Fig. 1).

Twisting the two phenyl rings from planarity, the allyl cation **Ia** is expected to have a structure in which the *p*-orbital of the middle carbon (2) overlaps with *p*-orbitals on both sides to permit delocalization of electrons. Thus, the predominant formation of 2,3-dihydro-1,4-benzoquinones **3c–e** can be ascribed to the less hindered environment at the carbon atom (1) than at the diphenyl-substituted carbon atom (3). Unlike that for cation **Ia**, a molecular model (CPK) of the biphenyl-2,2′-diyl-substituted allyl cation **Ib** showed that the central *p*-orbital cannot be aligned parallel to the *p*-orbital of carbon (3), because of the gross steric hindrance between the fluorenylidene

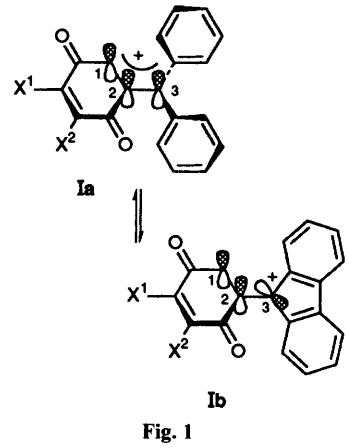



**Fig. 1**

*ortho*-hydrogen and the facing carbonyl oxygen atom as depicted in postulated compounds **9g**, **h**. Hence, the migration of halide to the carbon (3) appears to be the exclusive process. In conformity with this, the thermolysis products **8g**, **h** remained unchanged on extended storage at 100 °C (3 days).

*Thermolysis of Diphenylhomonaphthoquinones* **2a–c**.—Similar to bromo-substituted diphenylhomobenzoquinones **1c–e**, bromo-substituted diphenylhomonaphthoquinone **2c** was thermolysed ($t_{\frac{1}{2}}$ 3.65 h at 100 °C in benzene), to give 2-bromo-3-diphenylmethylene-2,3-dihydro-1,4-naphthoquinone **10** in quantitative yield (Scheme 2). The structure of compound **10** was established on the basis of the usual spectroscopic data as well as the chemical conversion of the compound into 2-[(α-

**Table 2** Thermolysis of bromo-substituted diphenylhomonaphthoquinone **2c** at 100 °C under various conditions

| Entry | Concentration (mol dm$^{-3}$) | Solvent[a] | Reaction time ($t$/day) | Method[b] | Yield (%)[c] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **10** | **11** | **12** | **13** (*meso*/±) | **14** | **15** | **16** | **17** |
| 11 | 0.50 | B | 7 | C | 31.2 | 15.2 | 5.4 | 0 | 15.6[d] | 18.3[d] | 6.5[d] | |
| 12 | 0.050 | B[e] | 1 | C | 100 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 13 | 0.050 | B[e] | 3 | C | 94.5 | 0 | 0 | 5.5 (3.4) | 0 | 0 | 0 | |
| 14 | 0.050 | B[e] | 7 | C | 90.1 | 0 | 0 | 9.9 (3.4) | 0 | 0 | 0 | |
| 15 | 0.050 | B[e] | 12 | C | 88.0 | 0 | 0 | 12.0 (3.4) | 0 | 0 | 0 | |
| 16 | 0.050 | B[e] | 20 | C | 84.1 | trace | trace | 15.9 (3.4) | 0 | 0 | 0 | |
| 17 | 0.50 | D | 7 | O | 39.0 | 0 | 0.5 | 54.4 (2.0) | 3.1 | 0 | 0 | |
| 18 | 0.50 | T | 7 | C | 12.0 | 4.5 | 42.5 | 0 | 34.5 | 0 | 0 | 38.0 |
| 19 | 0.050 | T | 7 | C | 8.0 | 0 | 43.5 | 6.0 (*meso* ≫ ±) | 24.8 | 0 | 0 | 38.8 |
| 20 | 0.50 | T | 7 | O | 8.6 | 0 | 0 | 84.0 (49) | 2.4 | 0 | 0 | 50.5 |

[a] B: benzene; D: decalin; T: toluene. [b] C: closed system; O: open system. [c] Unless otherwise noted, determined due to the integral proportions of the $^1$H NMR spectra relative to an internal standard, 1,1,1,2-tetrachloroethane. [d] Isolated yield. [e] [$^2H_6$]Benzene.

hydroxy and α-methoxy)diphenylmethyl]-1,4-naphthoquinones **18** and **18'** by treatment with methanol and water.* However, the methyl- and the chloro-substituted substrates **2a** and **2b** were unchanged after 1 week's heating under the same conditions.

In contrast to the xanthylium formation from bromo-substituted homobenzoquinones **1c–e**, bromo-substituted homonaphthoquinone **2c** revealed the different mechanistic features on prolonged heating to afford several products *via* the quinone **10** as shown in Scheme 2 and Table 2. Heating of compound **2c** in benzene at 100 °C for 7 days in a sealed glass tube produced 2-benzhydryl-3-bromo-1,4-naphthoquinone **11** (15.2%), 2-benzhydryl-1,4-naphthoquinone **12** (5.4%), and dimeric dihydrodioxadibenzopyrene derivative, $C_{46}H_{30}O_4$ **14** (15.6%) and its mono- and di-brominated products, **15** (18.3%) and **16** (6.5%), in addition to the primary product **10** (31.2%) (entry 11). Compound **14** and its dibrominated derivative **16** have a centre of symmetry as indicated by the presence of only 15 non-equivalent carbon atoms in their $^{13}$C NMR spectra.†

Mechanistically, compound **11** seems to be derived from a [1,3]-H shift of primary product **10**. Formation of compound **12** can be rationalized by generation of naphthoquinone-fused allyl radical **Ic** *via* thermal fission of the C–Br bond in compound **10**, followed by hydrogen abstraction. Indeed, the crystalline product **10** showed an electron spin resonance (ESR) signal at 130 °C, with its hyperfine structure suggesting a widely spread spin density (Fig. 2). Dimeric **14** comes from the precursor dimer **13**. Recently, we reported the formation of dimer **13** *via* monomer radical **Ic** from the reductive dimerization of compound **10** on treatment with zinc powder.[7i] Two molecules of the radical will combine to produce compound **13**.‡ The tetraone **13** will lead to hexacycle **14** by way of double intramolecular cyclization between carbonyl

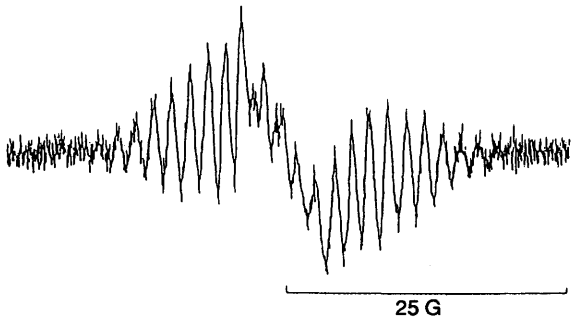



**Fig. 2** An EPR spectrum (centred at 3307.5 G) obtained on heating crystalline compound **10** at 132 °C

functions and diphenylmethylene double bond (*vide infra*). Compounds **15** and **16** can be assumed to result from sequential bromination of compound **14**, for substrate **14** was completely converted into dibromide **16** by way of monobromide **15** when kept at ambient temperature for 5 days in benzene containing a few drops of bromine.

When thermolysed in a one-tenth diluted concentration, bromide **2c** slowly gave the dimer **13** on stoichiometric consumption of the primary product **10**, though the expected products, **11**, **12**, **14**, **15** and **16**, were not detected during a period of up to 12 days (entries 12–15). The *meso*/± isomer quotient (3.4)§ of compound **13** did not change throughout the 20 days of thermolysis. These results imply that recombination of radical **Ic** certainly takes place and that product **13** can remain unchanged only under the very low concentration of HBr derived from bromination of some aromatic nuclei (*vide infra*). In fact, an isomeric mixture of **13** (*meso*/± 4.4) was completely recovered without any stereorandomization even when heated at 100 °C for 1 week in pure benzene. The negligible amount of HBr produced must be also responsible for the absence of the rearranged product **11** and the hydrogen-abstracted product **12**.

In contrast to the closed system, use of high boiling decalin allowed high (55%) yields of dimer **13** (*meso*/± 2.0) to be obtained under the open system, together with a small amount of compounds **12** and **14** (entry 17). Under these conditions, volatile $Br_2$ or HBr, if formed, will escape to depress the processes giving [1,3]-H-shifted bromo compound **11**, hydrogen-abstracted naphthoquinone **12**, and intramolecularly cyclized hexacycle **14**.

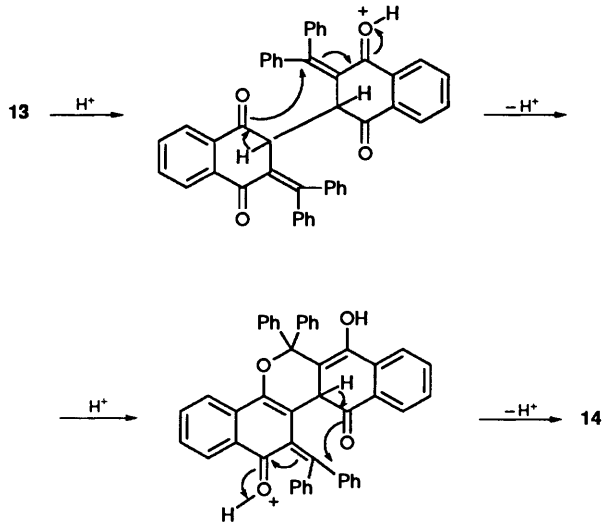
When thermolysed in radical-sensitive toluene, compound **2c** gave benzyl bromide **17** (38%), and compounds **10** (12%), **11**

* The structure of compound **10** was confirmed by X-ray diffraction analysis and will be published separately.

† Inspection of the $^1$H NMR spectrum of compound **16** also revealed that one β-hydrogen of the naphthoquinone framework is replaced by bromine, since the integral ratio due to the high-field β-hydrogens (δ 7.54–7.58, in $CDCl_3$) was reduced to half of that due to the low-field α-hydrogens (δ 8.10–8.20); these naphthoquinone hydrogens characteristically resonated to lower field than those of the diphenyl groups (δ 7.21–7.36). Unfortunately, which position of the two β-sites was replaced has not been defined yet.

‡ Recently, we also found that compound **10** was converted into dimer **13** when irradiated (> 330 nm) in the presence of triethylamine (TEA). This can be explained by considering the generation of the allyl radical **Ic** *via* photoelectron transfer from TEA followed by the release of $Br^-$. Details will be described elsewhere.

§ Stereochemistry of isomeric dimer **13** was previously determined on the basis of $^1$H NMR analysis using a chiral shift reagent; see ref. 7*i*.




Scheme 3

(4.5%), **12** (42.5%) and **14** (34.5%) with no detection of dimer **13** (entry 18). Formation of benzyl bromide **17** is unambiguous evidence supporting the radical processes. In toluene, bromination of compound **14** did not occur, since the generated bromine atom was quickly scavenged by the cage solvent to become benzyl bromide and HBr. Therefore, the absence of dimer **13** may be attributable to an HBr-catalysed cyclization to hexacycle **14** as shown in Scheme 3. This intermolecular conversion may be achieved by initial protonation of the outer carbonyl group followed by the attack of another carbonyl oxygen on the positively charged diphenylmethylene carbon atom. In support of this, compound **13** (*meso*/± 4.4), though stable when heated at 100 °C for a week in pure toluene, was quantitatively converted into compound **14** under the same conditions by addition of one drop of $Br_2$ and heating for 1 day. More noticeable is the formation of a large amount of hydrogen-abstraction product **12**. Two candidates seem to be possible hydrogen donors, *i.e.* toluene and HBr. The actual identity can be solved as follows.

Thermolysis in a one-tenth diluted solution achieved a comparable product distribution except for the appearance of a small amount of dimer **13** (6%; *meso* ≫ ±) and complete disappearance of bromide **11** (entry 19). The low concentration of the resulting HBr seems to be responsible for the incomplete cyclization of dimer **13** and the absence of [1,3]-H-shifted product **11**. From the fact that the yield of debrominated compound **12** is essentially the same as that obtained in the concentrated solution, one might be inclined to consider abstraction of hydrogen from the bulk toluene. However, toluene was not a true hydrogen donor. Thermolysis under an open system, in which gaseous HBr will be completely extruded gave no hydrogen-abstracted product **12** and hydrogen-shifted product **11**, but instead large amounts of dimer **13** (84%; *meso*: ± 49.1) along with small amounts of hexacycle **14** (entry 20). This finding is unequivocal evidence for the participation of HBr as a hydrogen source as well as a catalyst for the [1,3]-H shift. As a consequence, in the absence of HBr, the allyl radical **Ic** inevitably dimerizes to **13** (*e.g.*, entries 17 and 20).

*Thermolysis of Biphenyl-2,2'-diylhomonaphthoquinones* **2d–f**. —Bromo-1,4-naphthoquinone gave, spontaneously, cyclopropane-ring-opened 2-(9-bromofluoren-9-yl)-1,4-benzoquinone **19f** in its reaction with 9-DF at ordinary temperature. Chloro-substituted biphenyl-2,2'-diylhomonaphthoquinone **2e** was completely thermolysed to the similar 2-(9-chlorofluoren-9-yl)-1,4-naphthoquinone **19e** at 100 °C for 2 h, whereas the methyl-substituted **2d** was recovered unchanged even after 1 week of

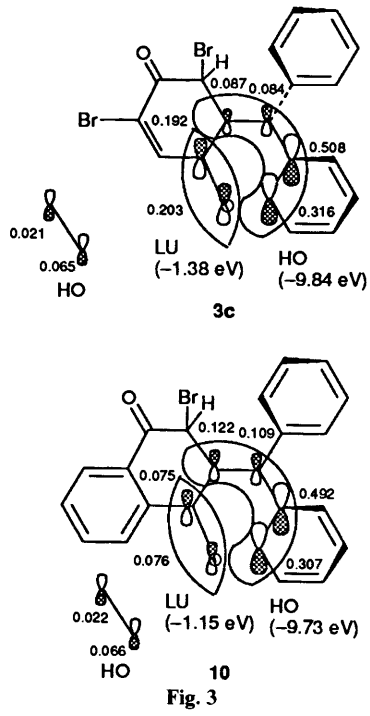



Fig. 3

heating at this temperature (Scheme 2). Compounds **19e** and **19f** remained intact even after 3 days of heating at 100 °C in benzene.

*Effects of the Quinone Moiety*.—Though the ring cleavage of fused cyclopropanes was much governed by the nature of the substituents ($X^3$), the rate of this first-stage reaction was little affected by changes in the quinone framework. For instance, the conversion of brominated homonaphthoquinone **2c** into compound **10** proceeded with a first-order rate constant of $5.27 \times 10^{-5}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 3.65 h) at 100 °C in benzene. This value is only about twice as large as that of the corresponding homobenzoquinone **1c** ($2.71 \times 10^{-5}$ $s^{-1}$, $t_{\frac{1}{2}}$ 7.10 h). It was also noted that the cyclization of compounds **3** to xanthylium ions **4** occurs readily as judged by the almost quantitative formation of salts **4** after 2–3 days of heating. By contrast, the intermediate **10** is resistant to such unimolecular cyclization, because a possible xanthylium salt was not detected even after heating for a long time (*e.g.*, entry 16).

Why does the intermediate **10** exhibit such remarkable persistency towards thermal cyclization to a xanthylium salt? At first[8] we rationalized the formation of xanthylium salts **4** in terms of the heat-promoted electrocyclization associated with the disrotatory motion of the relevant 6π HOMO of compounds **3**, just as in the hexa-1,3,5-triene→cyclohexadiene interconversion.[15] However, the straightforward application to intermediate **10** provided no satisfactory account for its thermal inertia, since the corresponding 6π HOMO of compound **10** is very similar to that of compound **3c** in both the size of the lobes and the orbital energy.* The HOMO part of each carbonyl function is separately shown on the left-hand side of the carbonyl group in Fig. 3.

This conflict can be resolved by relying on the FMO interactions between the HOMO of the diphenylmethylene moieties and the LUMO of the carbonyl functions as depicted for the intermediates **3c** and **10**. It can be easily recognized that

* Molecular orbital calculations by the PM3 method (ref. 16) were performed with the MOPAC program (ver. 6.0) using an Iris Indigo R4000 computer. The structural output was recorded by using the MOL-GRAPH program Ver. 2.8 by Daikin Industries, Ltd.

compound **3c** has the larger coefficients in the LUMO so that the charge-transfer participation from the HOMO of the diphenylmethylene moiety plays a significant role in its cyclization. The smaller size of the LUMO lobes of compound **10** may be ascribed to electron-donating participation of the fused-benzene nucleus. Of course, the LUMO–HOMO energy difference (8.48 eV) in compound **3c** is slightly more favourable for the orbital overlapping compared with that of compound **10** (8.58 eV). Accordingly, compound **3** will undergo an electrocyclization promoted by an intramolecular charge-transfer interaction, while the intermediate **10** would inevitably lead to the radical pathway owing to its poor orbital interaction. These frontier orbital considerations were well documented in a unified manner for various types of concerted processes.[17]

*Conclusions.*—In the present work, thermolysis of diphenyl- and biphenyl-2,2′-diyl-substituted homobenzoquinones **1** and homonaphthoquinones **2** with a substituent X[3] (Me, Cl, Br) has been described. It has been demonstrated that the biphenyl-2,2′-diylhomoquinones with the halogeno substituents were easily transformed into 2-(9-halogenofluoren-9-yl)-benzoquinones and -naphthoquinones *via* a cyclopropane ring cleavage. The diphenylhomoquinones were less labile and only bromo-substituted ones underwent cyclopropane-ring cleavage to provide different products, 2-bromo-3-diphenylmethylene-2,3-dihydro-benzoquinones **3c–e** and the -naphthoquinone **10**. The product change was explained by the structural nature of the diaryl substituents. It was found that compounds **3c–e** give xanthylium salts *via* 6π electrocyclization on further heating, whereas compound **10** gave dimeric and hydrogen-abstracted products by way of an allyl radical. The drastic effect of the quinone framework can be accounted for by an intramolecular FMO interaction.

## Experimental

All m.p.s were taken on a Yanagimoto micro-melting-point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were obtained on a JEOL EX-270 MHz instrument with $Me_4Si$ as internal standard. *J* Values are given in Hz. UV spectra were recorded on a Hitachi U-3400 spectrophotometer. Mass spectra were taken on a JEOL JMS DX303 mass spectrometer. Kinetic measurements by HPLC were carried out on a Hitachi 655A-12 liquid chromatograph equipped with a Waters RCM 8 × 10 module installing a Radial-Pak cartridge ($8C_{18}$, 5 μ). The reaction solutions for kinetic runs were prepared by mixing of an appropriate amount of cyclopropane and biphenyl (as an internal standard) in benzene and sealed in more than 10 glass capillaries of 1.8 mm diameter. The capillary tubes were immersed in a thermostatted bath (100 ± 0.05 °C, Haake EF thermostat) and after several minutes the reaction was monitored at regular time intervals by following the absorptions due to cyclopropane and biphenyl at 280 nm up to ~ 70% completion. The first-order rate constants ($k/s^{-1}$) were obtained from the slope of linear plots of natural logarithmic values of the relative absorptions *vs.* time.

*Materials.*—Benzene was refluxed for 1 day over lithium aluminium hydride and was then distilled. Toluene was refluxed over metal sodium and fractionated. Decalin (*cis/trans* mixture, extra pure) was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. All homoquinones **1a–g**, **2a–e** were prepared from the reactions of diazodiphenylmethane (DDM) and 9-DF with the corresponding quinones according to the procedure as described.[6] Homoquinones **1h** and **2f** were not obtained owing to their thermal lability to give ring-opened products **9h** and **19f**, respectively, even at ambient temperature (*vide infra*). Physical constants and spectral data of the prepared homoquinones **1a**, **c–f** and **2c** are given in Table 3; we do not report data for the known **1b**, **g**[6] **2a**, **d**,[18] and **2b**, **e**.[19]

*Thermolysis of* 2,3-*Diphenyl*-2,3-*dihydro*-2,3-*methano*-1,4-*benzoquinones* **1a–e**. *General Procedure.*—A solution of bromo-substituted compound **1c** (100 mg) in benzene (0.5 $cm^3$) was heated in a sealed glass tube (φ 5 mm) at 100 °C for 2 days to furnish, almost quantitatively, reddish orange crystals (97 mg, 97%) on the glass surface. Recrystallization from a large volume of acetonitrile gave 3-*bromo*-2-*hydroxy*-9-*phenylxanthylium bromide* **4c** as orange-red leaflets; m.p. 250 °C (decomp.); $\nu_{max}$(KBr)/$cm^{-1}$ 3435, 2873, 1620, 1507, 1453, 1263, 1204, 749 and 703; $\lambda_{max}$(MeCN)/nm 227 (log ε 4.40), 249 (4.36), 270 (4.42), 408 (4.53) and 491 (3.82); $\delta_H(CD_3OD)$ 6.69 (1 H, s) and 7.03–7.40 (10 H, m); *m/z* 351 ($M^+$ − Br) (Found: C, 53.0; H, 2.9. $C_{19}H_{12}Br_2O_2$ requires C, 52.81; H, 2.80%).

The NMR spectrum of compound **4c** in common aprotic solvents could not be obtained because of its insolubility. Aprotic solvents like methanol brought about nucleophilic attack at the 9-position of the xanthylium salt to afford a 9-methoxyxanthene derivative. Thus, the NMR spectrum in $CD_3OD$ is the spectrum of such a derivative. This is also the case for the other salts **4d** and **4e**.

Similar thermolysis of bromo-substituted substrates **1d** and **1e** for 3 days gave xanthylium salts **4d** and **4e** respectively. However, methyl- and chloro-substituted substrates **1a** and **1b** remained unchanged under similar conditions for 5 days.

4-*Bromo*-2-*hydroxy*-9-*phenylxanthylium bromide* **4d** (95%), red prisms (from acetonitrile), m.p. 340 °C (decomp.); $\nu_{max}$(KBr)/$cm^{-1}$ 3425, 1624, 1514, 1362, 1274, 1232, 761 and 701; $\delta_H(CD_3OD)$ 6.58 (1 H, d, *J* 2.97) and 7.05–7.32 (10 H, m); *m/z* 351 ($M^+$ − Br) (Found: C, 52.9; H, 2.85%).

3,4-*Dibromo*-2-*hydroxy*-9-*phenylxanthylium bromide* **4e** (96%), red prisms (from acetonitrile), m.p. 270 °C (decomp.); $\nu_{max}$(KBr)/$cm^{-1}$ 3439, 1613, 1579, 1495, 1378, 1261, 758 and 702; $\delta_H(CD_3OD)$ 6.74 (1 H, s) and 7.08–7.34 (9 H, m); *m/z* 429 ($M^+$ − Br) (Found: C, 44.65; H, 2.2. $C_{19}H_{11}Br_3O_2$ requires C, 44.56; H, 2.24%).

2,5-*Dibromo*-3-*diphenylmethylene*-2,3-*dihydro*-1,4-*benzoquinone* **3d**. A solution of compound **1d** (100 mg) in benzene (0.5 $cm^3$) was heated in a sealed glass tube at 100 °C for 1 day to provide crystalline compound **4d** (58 mg, 58%) on filtration. The filtrate was dried under reduced pressure to yield *title compound* **3d** (35 mg, 35%) and unchanged substrate **1d** (5 mg, 5% recovery). Fractional recrystallization from pentane–benzene gave pure compound **3d** as pale yellow prisms, m.p. 150 °C; $\nu_{max}$(KBr)/ $cm^{-1}$ 1688, 1492, 1446, 1266 and 704; $\delta_H(CDCl_3)$ 5.32 (1 H, d, *J* 1.65), 6.98 (1 H, d, *J* 1.65) and 7.01–7.45 (10 H, m); $\delta_C(CDCl_3)$ 49.88 (d), 127.3 (s), 128.4 (d), 128.8 (d), 128.9 (d), 129.3 (d), 129.4 (d), 130.1 (d), 137.2 (d), 138.5 (s), 139.9 (s), 144.4 (s), 158.5 (s), 181.1 (s) and 186.5 (s); *m/z* 351 ($M^+$ − Br) (Found: C, 53.0; H, 2.9. $C_{19}H_{12}Br_2O_2$ requires C, 52.81; H, 2.80%. This compound re-solidified as the xanthylium salt **4d** above 150 °C.

*Thermolysis of Compound* **1c** *in the Presence of Methanol.*—A solution of compound **1c** (100 mg) in methanol–benzene (1:4 by volume; 2 $cm^3$) was heated at 100 °C for 1 day in a sealed glass tube. The reaction mixture was concentrated, and chromatographed on silica gel to give successively 2-*bromo*-5-[*methoxy*-(*diphenyl*)*methyl*]-1,4-*benzoquinone* **7c** (88.5 mg, 89%) and unchanged substrate **1c** (8 mg, 8% recovery) with hexane–benzene (1:1 by volume) as eluent. Recrystallization of compound **7c** from hexane–benzene gave yellow needles, m.p. 127–128 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1663, 1588, 1448, 1183, 1067, 906 and 704; $\delta_H(CDCl_3)$ 2.92 (3 H, s), 7.04 (1 H, s), 7.33–7.45 (10 H, m) and 7.61 (1 H, s); *m/z* 382 ($M^+$) (Found: C, 62.7; H, 4.0. $C_{20}H_{15}BrO_3$ requires C, 62.68; H, 3.95%).

**Table 3** Physical constants and analytical data of homoquinones

| Compound | M.p. (*T*/°C) | Calc. (%) C | Calc. (%) H | Found (%) C | Found (%) H | *m/z* ($M^+$) | $^1$H NMR [a] |
|---|---|---|---|---|---|---|---|
| **1a** | 111–112 | 83.42 | 6.00 | 83.5 | 6.1 | 302 | 1.25 (3 H, s), 1.58 (3 H, d, *J* 1.65), 3.08 (1 H, s), 6.06 (1 H, d, *J* 1.65), 7.15–7.44 (10 H, m) |
| **1c** | 156–158 | 52.81 | 2.80 | 52.9 | 2.9 | 351 ($M^+$ − Br) | 3.73 (1 H, s), 6.90 (1 H, s), 7.12–7.61 (10 H, m) |
| **1d** | 151–152 | 52.81 | 2.80 | 53.0 | 2.9 | 351 ($M^+$ − Br) | 3.60 (1 H, d, *J* 1.65), 6.77 (1 H, d, *J* 1.65), 7.10–7.48 (10 H, m) |
| **1e** | 156–157 | 44.65 | 2.17 | 45.0 | 2.3 | 511 | 3.80 (1 H, s), 7.02–7.58 (10 H, m) |
| **1f** | 197–199 | 83.98 | 5.37 | 83.8 | 5.6 | 300 | 3.33 (1 H, s), 6.85 (1 H, d, *J* 1.32), 7.08–7.41 (6 H, m), 7.75–7.80 (2 H, m) |
| **2c** | 168–169 | 68.50 | 3.75 | 68.6 | 3.9 | 402 | 3.79 (1 H, s), 6.80–7.00 (3 H, m), 7.10–7.40 (5 H, m), 7.45–7.60 (4 H, m), 7.75–7.95 (2 H, m) |

[a] Measured in $CDCl_3$; $SiMe_4$ as internal standard.

*Reaction of Compound* **4c** *with Diazomethane in Methanol.*—To a stirred solution of compound **4c** (60 mg) in methanol (2 $cm^3$) was added an excess of ethereal diazomethane with evolution of nitrogen gas. After the mixture had been stored for 2 h, the solvent was evaporated off and the reaction mixture was subjected to column chromatography on silica gel to provide 3-*bromo*-2,9-*dimethoxy*-9-*phenylxanthene* **5c** (46 mg, 83%) with hexane–benzene (1 : 1). Recrystallization from hexane–benzene gave prisms, m.p. 115–117 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1477, 1394, 1227, 1049 and 753; $\delta_H$($CDCl_3$) 2.90 (3 H, s), 3.67 (3 H, s), 6.63 (1 H, s) and 6.90–7.47 (10 H, m); *m/z* 365 ($M^+$ − $OCH_3$) (Found: C, 63.4; H, 4.3. $C_{21}H_{17}BrO_3$ requires C, 63.49; H, 4.31%).

*Treatment of Compound* **5c** *with Perchloric Acid.*—To a solution of compound **5c** (46 mg) in acetonitrile (2 $cm^3$) was added perchloric acid (60 wt.%; 20 mg) with a rapid colour change to orange-red. After 0.5 h, the solvent was removed under reduced pressure to yield reddish granules (51 mg, 95%). Recrystallization from benzene–acetonitrile gave 3-*bromo*-2-*methoxy*-9-*phenylxanthylium perchlorate* **6c** as orange-red prisms, m.p. 248–250 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1619, 1501, 1477, 1426, 1121, 1087 and 754; $\lambda_{max}$(MeCN)/nm, 227 (log ε 4.39), 249 (4.33), 271 (4.38), 408 (4.48) and 492 (3.78) (Found: C, 51.55; H, 3.05. $C_{20}H_{14}BrO_6Cl$ requires C, 51.58; H, 3.03%).

*Thermolysis of* (*Fluorene*-9,9-*diyl*)-2,3-*dihydro*-1,4-*benzoquinones* **1f–h**.—The methyl-substituted compound **1f** was so stable as to be recovered unchanged after 1 week of heating at 100 °C in benzene.

The chloro-substituted compound **1g** was quantitatively converted into 2-*chloro*-5-(9-*chlorofluoren*-9-*yl*)-1,4-*benzoquinone* **8g** at 100 °C for 2 h in a sealed benzene solution. Recrystallization from hexane–benzene provided orange-yellow needles, m.p. 181–182 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1664, 997 and 738; $\delta_H$($CDCl_3$) 6.67 (1 H, s), 7.70 (1 H, s) and 7.24–7.83 (8 H, m); *m/z* 340 ($M^+$) (Found: C, 66.8; H, 2.9. $C_{19}H_{10}Cl_2O_2$ requires C, 66.88; H, 2.95%).

Bromo-substituted compound **h** could not be isolated from the reaction of 9-DF (463 mg) and 2,5-dibromo-1,4-benzoquinone (640 mg) in benzene (10 $cm^3$) at room temperature for 1 day because of its intrinsic thermal lability to give the ring-cleaved product 2-*bromo*-5-(9-*bromofluoren*-9-*yl*)-1,4-*benzoquinone* **8h** as orange-red needles (100%), m.p. 179–180 °C (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1661, 1589 and 737; $\delta_H$($CDCl_3$) 7.00 (1 H, s) and 7.23–7.51 and 7.73–7.90 (9 H, m); $\delta_C$($CDCl_3$) 62.7 (s), 121.0 (d), 124.8 (d), 128.6 (d), 129.7 (d), 136.2 (d), 136.6 (s), 138.8 (s), 139.0 (d), 147.2 (s), 147.3 (s), 179.9 (s) and 180.5 (s); *m/z* 430 ($M^+$) (Found: C, 53.1; H, 2.3. $C_{19}H_{10}Br_2O_2$ requires C, 53.00; H, 2.45%).

*Attempted Thermolysis of* 2,3-*Diphenylmethylene*-2,3-*dihydro*-1,4-*naphthoquinones* **2a**, **b**.—A solution of methyl-substituted compound **2a** (50 mg) in benzene (0.5 $cm^3$) was heated at 100 °C in a sealed glass tube for 7 days. Evaporation of the solvent left substrate **2a** unchanged. The chloro-substituted analogue **2b** also remained intact under the same conditions.

2-*Bromo*-3-*diphenylmethylene*-2,3-*dihydro*-1,4-*naphthoquinone* **10**.—A solution of compound **2c** (900 mg) in benzene (10 $cm^3$) was heated at 100 °C in a sealed glass tube for 24 h. Evaporation of the solvent provided an almost quantitative yield of *title product* **10** (by NMR spectroscopy). Recrystallization from hexane–benzene gave pale yellow prisms (77%), m.p. 170–171 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1683, 1583, 1565, 1325, 1284, 1245, 986 and 698; $\delta_H$($CDCl_3$) 5.53 (1 H, s), 7.00–7.06 (2 H, m), 7.22–7.46 (8 H, m), 7.77–7.85 (2 H, m) and 8.06–8.14 (2 H, m); $\delta_C$($CDCl_3$) 51.6, 127.2, 127.9, 128.2, 128.8, 129.0, 129.2, 129.4, 129.7, 130.6, 131.4, 134.4, 135.0, 135.8, 139.3, 140.9, 157.0, 187.0 and 188.0; *m/z* 323 ($M^+$ − Br) (Found: C, 68.5; H, 3.9. $C_{23}H_{15}BrO_2$ requires C, 68.50; H, 3.75%).

*Treatment of Compound* **10** *with Methanol and Water.*—To a stirred solution of **10** (100 mg) in benzene (2 $cm^3$) was added methanol (500 mg). After 1 h, evaporation of the solvent left yellow crystalline 2-[*methoxy*(*diphenyl*)*methyl*]-1,4-*naphthoquinone* **18** as yellow prisms in quantitative yield, m.p. 145–147 °C (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1667, 1653, 1594, 1302, 1255, 1071, 893 and 701; $\delta_H$($CDCl_3$) 2.96 (3 H s), 7.29–7.40 (6 H, m), 7.51–7.56 (4 H, m), 7.62–7.69 (3 H, m), 7.86–7.92 (1 H, m) and 8.01–8.09 (1 H, m); *m/z* 354 ($M^+$) (Found: C, 81.4; H, 5.3. $C_{24}H_{18}O_3$ requires C, 81.34; H, 5.12%).

Similar treatment with water gave 2-[*hydroxy*(*diphenyl*)*methyl*]-1,4-*naphthoquinone* **18'** as yellow prisms (91%), m.p. 154–155 °C (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 3443, 1663, 1590, 1339, 1301, 1251, 755 and 700; $\delta_H$($CDCl_3$) 5.10 (1 H, s, exchangeable with $CD_3OD$), 6.30 (1 H, s), 7.30–7.37 (10 H, m), 7.73–7.79 (2 H, m) and 8.02–8.09 (2 H, m); *m/z* 340 ($M^+$) (Found: C, 81.0; H, 5.0. $C_{23}H_{16}O_3$ requires C, 81.16; H, 4.74%).

*Prolonged Heating of Compound* **2c** *under Various Conditions.*—General procedure was represented for two typical runs, (a) closed and (b) open systems.

(a) *Under closed system in benzene* (*entry* 11). A solution of compound **2c** (100 mg) in benzene (0.5 $cm^3$) was sealed in a glass tube (φ 5 mm). After 1 week of heating at 100 °C, the reaction mixture was dried *in vacuo* and submitted for NMR analysis to determine the yields of products by using 1,1,1,2-tetrachloroethane ($\delta_H$ 4.27, $CDCl_3$) as internal standard. The amounts

of products **10**, **11** and **12** were easily estimated on the basis of the relative integral proportions due to their well resolved aliphatic protons with respect to the internal standard. The yields of compounds **14–16** could not be determined owing to the absence of appropriate signals in the aliphatic region.

Column chromatographic treatment on silica gel successively gave a mixture of compounds **14–16** (39 mg) with hexane–benzene (3:1 v/v), the rearrangement product **11** (14 mg, 14%), debromo compound **12** (4 mg, 5%), and the alcohol **18'** (25 mg, 30%, derived from hydrolysis of intermediate **10**) with increasing amounts of benzene in hexane (~60% volume). Compounds **14–16** were separated by HPLC which eluted these dimeric products in the order **14** (12.5 mg, 15.6%), **15** (16.5 mg, 18.3%), and **16** (6.5 mg, 6.5%) with 2% water in methanol.

(b) *Under an open system in toluene* (*entry* 20). A solution of compound **2c** (100 mg) in toluene (0.5 $cm^3$) was placed in a round-bottom flask with a reflux condenser and was heated at 100 °C for 1 week. The precipitates were filtered off and were found to be all *meso*-**13** (35 mg, 44%) by NMR spectroscopy. The filtrate was concentrated to dryness and the residue was submitted for NMR measurement to determine the product yields as above. The reaction mixture was subjected to column chromatography on silica gel to afford, successively, benzyl bromide **17** (19 mg, 45%) with hexane, hexacycle **14** (1.5 mg, 1.9%), the alcohol **18'** (7 mg, 8%, derived from hydrolysis of compound **10**), dimer (±)-**13** (1.3 mg, 1.6%), a second crop of *meso*-**13** (27 mg, 34%) with increasing amounts of benzene in hexane (~100%).

2-*Bromo*-3-*diphenylmethyl*-1,4-*naphthoquinone* **11**, m.p. 187–188.5 °C; yellow prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1671, 1590, 1561, 1278, 719 and 704; $\delta_H$($CDCl_3$) 6.18 (1 H, s), 7.25–7.36 (10 H, m), 7.70–7.73 (2 H, m), 8.00–8.07 (1 H, m) and 8.14–8.17 (1 H, m); $\delta_C$($CDCl_3$) 54.91 (d, $J_{CH}$ 128), 126.9, 127.4, 127.5, 128.5, 129.1, 130.7, 131.8, 133.9, 134.3, 139.5, 141.8, 151.3, 178.0 and 181.4; *m/z* 323 ($M^+$ − Br) (Found: C, 68.65; H, 4.1. $C_{23}H_{15}BrO_2$ requires C, 68.50; H, 3.75%).

2-*Diphenylmethyl*-1,4-*naphthoquinone* **12**, m.p. 188–190 °C, yellow prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1656, 1591, 1330, 1304 and 699; $\delta_H$($CDCl_3$) 5.83 (1 H, s), 6.51 (1 H, s), 7.16–7.36 (10 H, m), 7.71–7.74 (2 H, m) and 8.03–8.08 (2 H, m); $\delta_C$($CDCl_3$) 50.1 (d, $J_{CH}$ 130), 126.1, 127.0, 127.1, 128.3, 128.8, 129.0, 132.0, 132.2, 133.8, 137.1, 140.2, 153.5, 184.3 and 185.2; *m/z* 324 ($M^+$) (Found: C, 85.3; H, 5.2. $C_{23}H_{16}O_2$ requires C, 85.16; H, 4.97%).

(±)- *and* meso-2,2'-*Bi*-(3-*diphenylmethylene*-2,3-*dihydro*-1,4-*naphthoquinone*) (±)- *and* meso-**13**. Identification of these compounds was described elsewhere.[7i]

6,6,13,13-*Tetraphenyl*-6,12-*dihydro*-5,11-*dioxadibenzo*[b,i]-*pyrene*-7,14-*diol* **14**, m.p. 327–329 °C, prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 3507, 1630, 1589, 1367, 1077, 984, 762 and 699; $\delta_H$($CDCl_3$) 4.69 (2 H, s, exchangeable with $CD_3OD$), 7.18–7.53 (24 H, m), 8.03 (2 H, d, *J* 8.25) and 8.27 (2 H, d, *J* 8.25); $\delta_C$($CDCl_3$) 85.4, 111.9, 113.0, 121.4, 122.9, 125.6, 126.1, 126.3, 126.8, 128.6, 128.7, 128.8, 139.0, 142.1 and 143.0; *m/z* 646 ($M^+$) (Found: C, 85.7; H, 5.0. $C_{46}H_{30}O_4$ requires C, 85.43; H, 4.68%).

2- (*or* 3-)*Bromo*-6,6,13,13-*tetraphenyl*-6,13-*dihydro*-5,12-*dioxadibenzo*[b,i]*pyrene*-7,14-*diol* **15**, m.p. 358–360 °C, prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 3492, 1582, 1368, 1080, 986 and 699; $\delta_H$($CDCl_3$) 4.68 (2 H, s, exchangeable with $CD_3OD$), 7.22–7.57 (23 H, m), 8.04 (1 H, d, *J* 8.25), 8.12 (1 H, d, *J* 8.91), 8.20 (1 H, d, *J* 1.98) and 8.26 (1 H, d, *J* 8.58); $\delta_C$($CDCl_3$) 85.3, 85.6, 111.6, 112.5, 112.7, 114.3, 120.0, 121.4, 122.9, 123.2, 124.7, 125.6, 125.8, 126.3, 126.9, 127.1, 128.3, 128.6, 128.67, 128.68, 128.7, 128.8, 128.9, 130.0, 139.0, 139.2, 141.8, 141.9, 142.2 and 143.2; *m/z* 724 ($M^+$) (Found: C, 76.2; H, 4.25. $C_{46}H_{29}BrO_4$ requires C, 76.14; H, 4.03%). In the $^1H$ NMR spectrum, the two hydroxy groups showed only one peak, at $\delta_H$ 4.68; however, methylation of these hydroxy functions with diazomethane differentiated between them as indicated by the appearance of two methoxy signals (see below).

2,9- (*or* 3,10-)*Dibromo*-6,6,13,13-*tetraphenyl*-6,13-*dihydro*-5,12-*dioxadibenzo*[b,i]*pyrene*-7,14-*diol* **16**, m.p. 350–352 °C, prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 3504, 1578, 1359, 1083, 988 and 699; $\delta_H$($CDCl_3$) 4.67 (2 H, s, exchangeable with $CD_3OD$), 7.21–7.36 (20 H, m), 7.57 (2 H, dd, *J* 8.91 and 1.98), 8.12 (2 H, d, *J* 8.91) and 8.20 (2 H, d, *J* 1.98); $\delta_C$($CDCl_3$) 85.5, 112.2, 114.0, 120.2, 123.2, 124.7, 125.6, 127.3, 128.6, 128.8, 129.0, 130.2, 139.1, 141.5 and 142.3; *m/z* 802 ($M^+$, Br) (Found: C, 68.95; H, 3.8. $C_{46}H_{28}Br_2O_4$ requires C, 68.67; H, 3.51%).

*Treatment of Diol* **15** *with Diazomethane*.—To a solution of diol **15** (20 mg) in benzene (0.5 $cm^3$) was added an excess of ethereal diazomethane. After 6 h, evaporation of the solvent provided a resinous product. Column chromatographic treatment on silica gel [hexane–benzene (1:1)] gave 85% yield of 2- (or 3-)*bromo*-7,14-*dimethoxy*-6,6,13,13-*tetraphenyl*-6,13-*dihydrodibenzo*[b,i]*pyrene* **20**, m.p. 205–206 °C, prisms (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1582, 1446, 1358, 1346, 1086, 1011 and 697; $\delta_H$($CDCl_3$) 2.96 (3 H, s), 2.98 (3 H, s), 7.13–7.27 (20 H, m), 7.38–7.50 (2 H, m), 7.54 (1 H, dd, *J* 8.91 and 1.98), 7.87 (1 H, dd, *J* 8.25 and 1.32), 8.00 (1 H, d, *J* 1.98), 8.19 (1 H, d, *J* 8.91) and 8.33 (1 H, dd, *J* 8.25 and 1.32); *m/z* 752 ($M^+$) (Found: C, 76.65; H, 4.6. $C_{48}H_{33}BrO_4$ requires C, 76.49; H, 4.41%).

*Thermolysis of* 2,3-*Fluorene*-9,9-*diyl*-2,3-*dihydro*-1,4-*naphthoquinones* **2d–f**.—The methyl-substituted compound **2d** was recovered unchanged even after 1 week of heating at 100 °C in a sealed glass tube in benzene.

2-(9-*Chlorofluoren*-9-*yl*)-1,4-*naphthoquinone* **19e**. Thermolysis of compound **2e** (300 mg) in benzene (5 $cm^3$) was carried out at 100 °C for 2 h in a sealed glass tube. Successive concentration of the solvent provided the yellow crystalline compound **19e** (97%) as yellow prisms, m.p. 201–202 °C (from hexane–benzene); $\nu_{max}$(KBr)/$cm^{-1}$ 1670, 1662, 1589, 1307 and 736; $\delta_H$($CDCl_3$) 7.25–8.23 (13 H, m); *m/z* 321 ($M^+$ − Cl) (Found: C, 77.25; H, 3.55. $C_{23}H_{13}ClO_2$ requires C, 77.42; H, 3.67%).

2-(9-*Bromofluoren*-9-*yl*)-1,4-*naphthoquinone* **19f**. Equimolar reaction of 2-bromonaphthoquinone (500 mg) with 9-DF (405 mg) in benzene (5 $cm^3$) for 1 day at room temperature provided *title compound* **19f** in almost quantitative yield. Recrystallization from hexane–benzene gave yellow prisms (96%), m.p. 213–214 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1663, 1589, 1447, 1334, 1308, 1252, 734 and 709; $\delta_H$($CDCl_3$) 7.27–8.07 (13 H, m); $\delta_C$($CDCl_3$) 64.4, 120.9, 124.6, 126.0, 127.2, 128.3, 128.5, 129.4, 131.8, 132.6, 133.8, 134.1, 138.8, 139.7, 148.3, 148.5, 181.1 and 185.3; *m/z* 321 ($M^+$ − Br) (Found: C, 68.9; H, 3.4. $C_{23}H_{13}BrO_2$ requires C, 68.84; H, 3.27%).

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## References

1 *The Chemistry of the Cyclopropyl Group*, ed. Z. Rappoport, Wiley, New York, 1987, vols. 1 and 2; H. N. C. Wong, M.-Y. Hon, C.-W. Tse and Y.-C. Yip, *Chem. Rev.*, 1989, **89**, 165; A. De Meijere, *Bull. Soc. Chim. Belg.*, 1984, **93**, 241; M. Murakami and S. Nishida, *Yuki Gosei Kagaku Kyokaishi*, 1983, **41**, 22 (*Chem. Abstr.*, 1983, **98**, 160267u); J. Salaün, *Chem. Rev.*, 1983, **83**, 619; S. Danishefsky, *Acc. Chem. Res.*, 1979, **12**, 66.

2 W. E. Parham and E. E. Schweizer, *Org. React.*, 1963, **13**, 55; D. C. Duffey, J. P. Minyard and R. H. Lane, *J. Org. Chem.*, 1966, **31**, 3865; P. v. R. Schleyer, T. M. Su, M. Saunders and J. C. Rosenfeld, *J. Am. Chem. Soc.*, 1969, **91**, 5174; C. B. Reese and A. Shaw, *J. Am. Chem. Soc.*, 1970, **92**, 2566.
3 C. H. DePuy, L. G. Schnack, J. W. Hausser and W. Wiedemann, *J. Am. Chem. Soc.*, 1965, **87**, 4006; C. H. DePuy, L. G. Schnack and J. W. Hausser, *J. Am. Chem. Soc.*, 1966, **88**, 3343; P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf and J. Paust, *J. Am. Chem. Soc.*, 1966, **88**, 2868.
4 W. Kirmse and H. Schütte, *J. Am. Chem. Soc.*, 1967, **89**, 1284.
5 R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395; C. H. DePuy, *Acc. Chem. Res.*, 1968, **1**, 33.
6 T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2507; 1989, **62**, 2580.
7 (*a*) G. W. Jones, D. R. Kerur, T. Yamazaki and H. Shechter, *J. Org. Chem.*, 1974, **39**, 492; (*b*) K. Maruyama and S. Tanioka, *J. Org. Chem.*, 1978, **43**, 310; (*c*) A. Osuka, H. Schimizu, H. Suzuki and K. Maruyama, *Chem. Lett.*, 1982, 329; (*d*) A. Osuka, M. H. Chiba, H. Schimizu and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1980, 919; (*e*) A. Osuka, H. Schimizu, H. Suzuki and K. Maruyama, *Chem. Lett.*, 1987, 1061; (*f*) T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3865; (*g*) T. Shingaki, H. Kuma, Y. Kusi and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 444; (*h*) T. Oshima and T. Nagai, *Chem. Lett.*, 1993, 1977; (*i*) H. Moriwaki, T. Oshima and T. Nagai, *J. Chem. Soc., Chem. Commun.*, 1994, 255.
8 Some of these results have been published in preliminary form; T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1993, **34**, 649.
9 R. A. McClelland, N. Banait and S. S. Steenken, *J. Am. Chem. Soc.*, 1989, **111**, 2929.
10 S. Wawzonek, *Heterocyclic Compounds*, ed. R. C. Elderfield, Wiley, New York, 1951, vol. 2, p. 472; J. Staunton, *Comprehensive Organic Chemistry*, ed. P. G. Sammes, Pergamon Press, London, 1979, vol. 4, p. 625.
11 E. N. Marvell, G. C. T. A. Gosink and G. Zimmer, *J. Am. Chem. Soc.*, 1966, **88**, 619. For photochemical cyclization of dienone systems, see K. R. Huffman and E. F. Ullman, *J. Am. Chem. Soc.*, 1967, **89**, 5629; R. P. Gandhi and R. C. Aryan, *J. Chem. Soc., Chem. Commun.*, 1988, 1024; T. H. Kim, Y. Hayashe and S. Isoe, *Chem. Lett.*, 1983, 651; T. H. Kim, Y. Asaka and T. Kubota, *Chem. Express*, 1991, **6**, 133.
12 C. F. Wilcox, L. M. Loew and R. Hoffmann, *J. Am. Chem. Soc.*, 1973, **95**, 8192; M. D. Harmony, S. N. Mathur, J.-I. Choe, M. Kattija-Ari, A. E. Howard and S. W. Staley, *J. Am. Chem. Soc.*, 1981, **103**, 2961; M. E. Jason, J. C. Gallucci and J. A. Ibers, *Isr. J. Chem.*, 1981, **21**, 95.
13 S. R. Sandler, *J. Org. Chem.*, 1967, **32**, 3877.
14 W. R. Moore, W. R. Moser and J. E. LaPrade, *J. Org. Chem.*, 1963, **28**, 220.
15 E. N. Marvell, G. Caple and B. Schatz, *Tetrahedron Lett.*, 1965, 385; E. Vogel, W. Grimme and E. Dinné, *Tetrahedron Lett.*, 1965, 391.
16 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
17 K. Fukui, *Acc. Chem. Res.*, 1971, **4**, 57; I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York, 1976.
18 F. M. Dean, P. G. Jones, R. B. Morton and P. S. Sidisunthorn, *J. Chem. Soc.*, 1963, 5336.
19 Y. Nakano, M. Hamaguchi and T. Nagai, *J. Org. Chem.*, 1989, **54**, 1135.

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