Addition of Diphenyldiazomethane to Unsubstituted and Chloro-Substituted 1,4-Benzoquinones. Effects of Chloro Substituents on the Addition Modes

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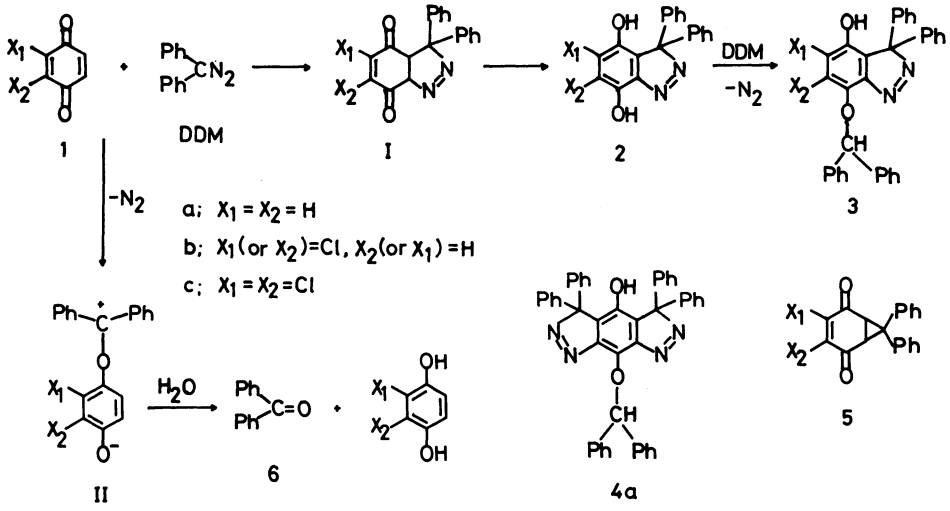
Unsubstituted 1,4-benzoquinone (**1a**) reacted with diphenyldiazomethane (DDM) at the C=C double bonds to give dihydroxy-3*H*-indazole (**2a**) and its benzhydryl ether (**3a**) together with benzodipyrazole derivative (**4a**). Similarly, reactions of 2-chloro- and 2,3-dichloro-1,4-benzoquinones (**1b** and **1c**) with DDM yielded the corresponding dihydroxy-3*H*-indazoles (**2b**, **2b'**, and **2c**) and their benzhydryl ethers (**3b**, **3b'**, and **3c**) along with 5—13% benzophenone (**6**). On the other hand, reaction of 2,6-dichloro-1,4-benzoquinone (**1e**) with DDM gave bicyclic **5e** and tricyclic diones (**7e**), together with benzophenone dimethyl acetal (**9**) in the presence of added methanol. In the same conditions, 2,3,5-trichloro-1,4-benzoquinone (**1f**) provided bicyclic dione (**5f**) and **9**. Formation of **6** and **9** was interpreted as arising from the hydrolysis and methanolysis of the 1:1 betaine intermediates given by the addition of DDM to the quinonoid C=O double bonds. The C=O addition increased with increasing chlorine substituents.

Additions of diazoalkanes to quinones are of synthetic and mechanistic interest because quinones, with the conjugated C=C and C=O double bonds, show two possible modes of addition which are markedly affected by the substituents and structural natures of these reactants, affording various types of products.[1] Diphenyldiazomethane (DDM), one of the most familiar diazoalkanes, is reported to add only to the C=C double bond of 1,4-benzoquinone (**1a**) giving 3*H*-indazole derivative **2a**.[2] Recently, it has been found that DDM reacts with 2,5-dichloro-1,4-benzoquinone (**1d**) at the C=C and C=O double bonds to yield bicyclic dione **5d** and poly(2,5-dichlorohydroquinone benzhydryl ether), respectively.[3] Further, tetrachloro-1,4-benzoquinone (**1g**) is known to undergo the addition of DDM only at the C=O double bond to afford poly(tetrachlorohydroquinone benzhydryl ether).[4] These striking changes in the reaction fashions with increasing chlorine substituents of 1,4-benzoquinones prompted us to extend the reaction of DDM to all of other chloro-substituted 1,4-benzoquinones. In this paper, we wish to report a systematic investigation of the products of reaction of DDM with 2-chloro-, 2,3- and 2,6-dichloro-, and 2,3,5-trichloro-1,4-benzoquinones, together with a reinvestigation of the product in the prior study of DDM and unsubstituted 1,4-benzoquinone. The effects of the substitution patterns of the chlorines on the addition modes of these quinones are also discussed.

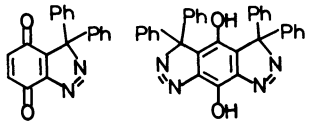
Results and Discussion

Reaction of DDM with 1,4-Benzoquinone (1a), 2-Chloro- (1b) and 2,3-Dichloro-1,4-benzoquinone (1c). In 1931 Fieser and his co-worker have reported that DDM adds to 1,4-benzoquinone (**1a**) to give in nearly quantitative yield dihydroxy-3*H*-indazole (**2a**).[2] However, besides **2a** (40%), two additional products, benzhydryl ether **3a** (39%) of **2a** and bis(3*H*-pyrazole) adduct **4a** (9%), were obtained in the present equimolar reaction in same benzene solution at 25 °C (Scheme 1).



Scheme 1.

This reaction consists in dipolar addition of DDM to **1a** and dienolization of the first product, pyrazoline (**Ia**). The compound **3a** appears to be the secondary product formed from the resulting **2a** and DDM. Indeed, equimolar reaction of **2a** and DDM yielded **3a** in 77% yield. Here, it seems likely that DDM prefers the unhindered phenolic OH of **2a** to avoid the steric repulsion due to the bulky diphenylmethylene moiety. With respect to the formation of **4a**, two possible routes can be put forward. One is the dehydrogenative conversion of **Ia** and/or **2a** into a 3*H*-indazole-4,7-dione (**III**) which would undergo addition of DDM to lead a precursor **IV** of **4a** after dienolization. Another



III IV

one is direct addition of DDM to **Ia** followed by dehydrogenation and dienolization yielding **IV**. The symmetric orientation of **4a** was established by the ^{13}C NMR spectrum which contains six signals for the twelve unprotonated C-atoms of the aromatic rings and one signal for the two diphenyl-substituted C-atoms of the 3*H*-pyrazole rings, respectively; asymmetric one would require nine and two signals for the corresponding C-atoms.

Similarly, equimolar reaction of DDM with **1b** and **1c** gave two principal products, 3*H*-indazole derivatives (**2b**, its regioisomer **2b′**, and **2c**) and their benzhydryl ethers (**3b**, **3b′**, and **3c**), together with 5—13% amounts of benzophenone (**6**) (Scheme 1). The **1b**, as expected, allowed the two addition direction at the unchlorinated C=C bond and thus provided the two sets of isomers, **2b** and **2b′**, **3b** and **3b′**. Each of the isomers could be isolated by column chromatography on silica gel, but it is not yet possible to make the structural assignments. In contrast with the above unchlorinated **1a**, these chlorinated **1b** and **1c** afforded **6**; the yield of **6** for dichlorinated **1c** was nearly twice that for the monochlorinated **1b**. The origin of **6** appears to be water-sensitive 1 : 1 betaine intermediates **II** given by addition of DDM to the C=O double bond. Such hydrolyzable betaines were the key intermediates in the previous reactions of DDM with tetrachloro-1,4-benzoquinone (**1g**)[4] and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),[5] where the additions take place only at the C=O bonds. It is also noted that the chlorinated C=C bonds of **1b** and **1c** remain intact for the dipolar addition of DDM. According to FMO (Frontier Molecular Orbital) theory, cycloadditions of simple diazoalkanes to electron-deficient olefins are classified as being controlled by the interaction of the highest occupied molecular orbitals (HOMOs) of diazoalkanes and the lowest unoccupied molecular

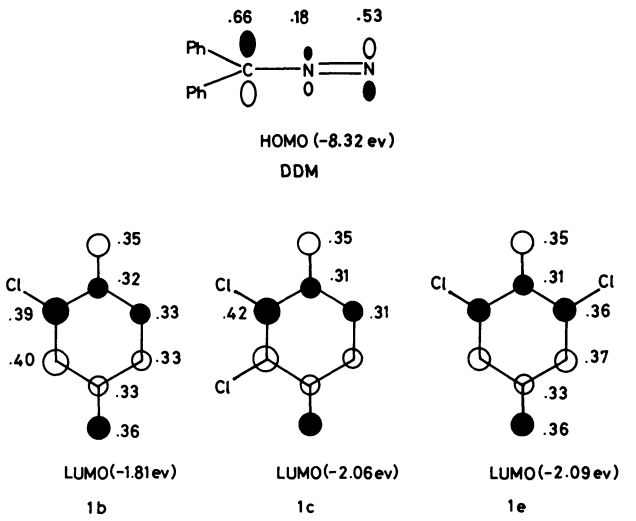


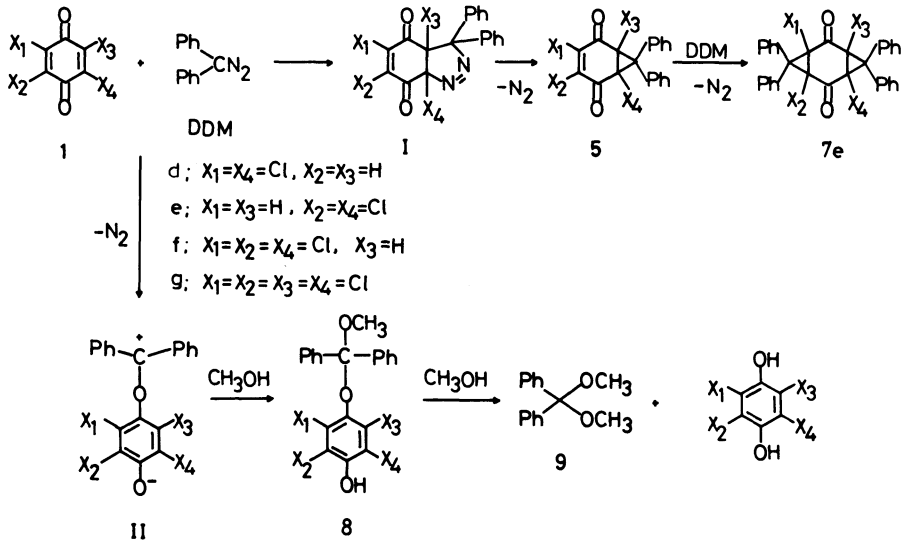
Fig. 1. MNDO π-orbital shapes and energies (in parentheses) of DDM and of 2-chloro-(**1b**), 2,3-dichloro-(**1c**), and 2,6-dichloro-1,4-benzoquinones (**1e**). Only coefficients of diazo function are shown for DDM.

orbitals (LUMOs) of olefins.[6] Figure 1 denotes the HOMO of DDM and LUMO of some quinones by MNDO calculation.[7] The concept of FMO predicts addition of DDM to the chloro-substituted C=C bonds rather than to the unsubstituted ones of **1b** and **1c**, because of the larger LUMO coefficients. This discrepancy is apparently attributable to the steric repulsion due to the chlorine substituents.

It has been found that, in refluxing benzene, these reaction systems of DDM and quinones **1a—c** showed no substantial changes in the product distributions except the formation of small amounts of nitrogen free bicyclic diones, **5a** (12%), **5b** (15%), and **5c** (5%). The **5a—c** supposedly arise by nitrogen release from **I** or by addition of diphenylcarbene to **1a—c**.[8]

Reaction of DDM with 2,6-Dichloro- (1e) and 2,3,5-Trichloro-1,4-benzoquinones (1f). We have previously reported that DDM and 2,5-dichloro-1,4-benzoquinone (**1d**) yield bicyclic dione **5d** and hydroquinone acetal (**8d**) in the presence of added methanol,[3] as shown in Scheme 2. The **5d** is the product given by loss of nitrogen from the initial dipolar adduct, pyrazoline (**Id**), whose chloro substituent prohibits the rearrangement into 3*H*-indazole derivative. While, the **8d** can be accounted for on the basis of a 1:1 betaine intermediate **IId**. Here, methanol was added as a capture of **IId**, otherwise, **IId** tends to polymerize into poly(2,5-dichlorohydroquinone benzhydryl ether).[3]

A study has now been made of reactions of DDM with 2,6-dichloro- (**1e**) and 2,3,5-trichloro-1,4-benzoquinones (**1f**), both of which are designed to avoid dienolization upon the dipolar addition to the C=C bonds as well as above **1d**. In the presence of 5 equiv of methanol, quinone **1e** reacted with DDM to give



Scheme 2.

Table 1. Effects of the Chloro Substituents on the Addition Modes of 1,4-Benzoquinones (**1a—g**) to DDM in Benzene

Quinone	Temp/°C	Substituted position	Addition mode/%	
			C=C addition	C=O addition
1a	25	—	100	0
1a	80	—	100	0
1b	25	2-	91[a]	9
1b	80	2-	90[a]	10
1c	25	2,3-	78[a]	22
1c	80	2,3-	83[a]	17
1d[b]	30	2,5-	49	51
1e	25	2,6-	50[c]	50
1f	25	2,3,5-	40[d]	60
1g[e]	30	2,3,5,6-	0	100

a) For unchlorinated C=C bond. b) Ref. 3. c) Estimated as the sum of **5e** and **7e**. d) For monochlorinated C=C bond. e) Solvent: tetrahydrofuran, see Ref. 4.

bicyclic dione **5e** (43%) and tricyclic dione **7e** (5%) in addition to benzophenone dimethyl acetal **9** (45%). Apparently, the behavior of **1e** is different from that of above **1d** in that the former involved the dipolar addition to both the C=C bonds to give **7e** and caused the redoxical acetalization into **9** and 2,6-dichlorohydroquinone. Indeed, bicyclic dione **5e** reacted slowly with DDM to provide **7e**; $k=1.57\times10^{-4}/s^{-1}\,mol^{-1}$ (30 °C, benzene). This value of k is only one twentieth of the overall rate ($k=3.36\times10^{-3}$) for the reaction of DDM and **1e**,[9] reflecting the above product distribution. However, **5d** derived from **1d** remained unchanged even on 2 day's standing with DDM under the same conditions. The stereochemistry of tricyclic dione **7e** is unknown. The ^1H NMR spectrum of **7e** ($\delta=2.66$, s, two bridgehead H) can not allow the stereochemical assignment in view of the fact that the corresponding protons of similar tricyclic diones, *syn*- and *anti*-tricyclo[5.1.0.$0^{3,5}$]octane-2,6-diones, do not resonate with each other.[10]

As for the process giving the 1:1 betaine **IIe**, it is more likely that DDM preferably attacks the C=O bond meta to the chloro-substituents in the light of the steric effects and of the results of the MNDO calculation[7] of **1e** which indicates slightly larger LUMO coefficients for this meta C=O bond (Fig. 1). Such an addition appears to be responsible for the higher reactivity of **8e**, because the combination of two meta chlorine substituents do make the diphenylmethylene moiety more positive than do the combination of ortho and meta chlorine-substituents in the comparable **8d**.

Introduction of one more chlorine atom to the quinone nucleus of **1e** brought about slight increase of the relative reactivity of the C=O to the C=C bonds, as exhibited by the product ratio (55:37) of acetal **9** to bicyclic dione **5f** for the reaction of 2,3,5-trichloro-1,4-benzoquinone (**1f**).

The product distributions are shown in Table 1. This table clearly shows the increase of C=O additions

with increasing Cl substituents as well as the lack of temperature effects (i.e., **1a—c**).

Experimental

All the melting points were uncorrected. The IR, ^{1}H NMR, ^{13}C NMR, and mass spectra were recorded on a Perkin Elmer 983 G, a Varian EM 390, a Hitachi 90 H, and a Hitachi RMU 6E spectrometers respectively.

Materials. The diphenyldiazomethane (DDM) was prepared by the oxidation of benzophenone hydrazone with yellow mercury oxide and recrystallized from petroleum ether; mp 29—30 °C. All quinones were purified before use by column chromatography on silica gel (hexane–benzene (3:1) as an eluent) and recrystallization from a mixture of hexane and benzene. The 1,4-benzoquinone (**1a**) and 2-chloro-1,4-benzoquinone (**1b**) were of commercial origin; mp 113—115 °C and 57—58 °C respectively. The 2,3-dichloro- (**1c**) and 2,6-dichloro-1,4-benzoquinone (**1e**), and 2,3,5-trichloro-1,4-benzoquinone (**1f**) were prepared according to the literature methods; mp 100—101 °C (lit,[11] 100—101 °C), 121—122 °C (lit,[12] 120.5—121 °C), and 167—168 °C (lit,[13] 169—170 °C) respectively.

4,7-Dihydroxy-3,3-diphenyl-3*H*-indazole (2a), 7-Benzhydryloxy-4-hydroxy-3,3-diphenyl-3*H*-indazole (3a), and 8-Benzhydryloxy-3,6-dihydro-4-hydroxy-3,3,5,5-tetraphenylbenzo[1,2-*c*:5,4-*c*']dipyrazole (4a). To begin with, it should be kept in mind that all the yields are based on DDM used. A benzene solution (10 ml) of DDM (540 mg, 2.78 mmol) and 1,4-benzoquinone **1a** (300 mg, 2.78 mmol) was allowed to stand for 10 h at 25 °C. The solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (20 to 100%) gave successively recovered **1a** (20 mg), **4a** (55 mg, 9%), and **3a** (255 mg, 39%). Further elution with benzene–ether (10%) yielded **2a** (339 mg, 40%). Recrystallization of **2a** from a mixture of hexane and ether gave yellow crystals: mp 208—209 °C (lit,[2] 210 °C); IR (KBr) 3405, 1501, 1454, 1272, 696 cm^{-1}; ^{1}H NMR (acetone-d_6) δ=6.60 (s, 1H, aromatic H), 6.87 (s, 2H, aromatic H), 7.2—7.5 (m, 9H, aromatic H), 8.23 (s, 1H, OH, exchangeable with CD_3OD), 9.07 (s, 1H, OH, exchangeable with CD_3OD); MS, *m/z* 302 (M^+). Anal. ($C_{19}H_{14}O_2N_2$) C, H, N. The compound **3a** was recrystallized from a mixture of hexane and benzene: mp 188—190 °C, yellow plates; IR (KBr) 3423, 1500, 1274, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.80 (s, 1H, OH, exchangeable with CD_3OD), 6.6—7.6 (m, 23H, aromatic H+$Ph_2C\underline{H}$); MS, *m/z* 468 (M^+). Anal. ($C_{32}H_{24}O_2N_2$) C, H, N. Recrystallization of **4a** from a mixture of hexane and benzene provided pale yellow prisms: mp 201—203 °C; IR (KBr) 3534, 1490, 1185, 1022, 754, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.50 (s, 1H, OH, exchangeable with CD_3OD), 6.9—7.8 (m, 30H, aromatic H), 7.93 (s, 1H, $Ph_2C\underline{H}$); ^{13}C NMR ($CDCl_3$) δ=87.1 ($Ph_2\underline{C}H$), 101.8 ($Ph_2\underline{C}$=), 127.0, 127.5, 127.9, 128.1, 128.5, 128.9 (protonated aromatic C), 134.7, 135.9, 138.8, 140.7, 141.3, 150.5 (unprotonated aromatic C); MS, *m/z* 660 (M^+). Anal. ($C_{45}H_{32}O_2N_2$) C, H, N.

7,7-Diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (5a). To a refluxing benzene (5 ml) containing **1a** (300 mg, 2.78 mmol) was added dropwise over 10 min a benzene solution (5 ml) of DDM (540 mg, 2.78 mmol). After 1 h refluxing, the solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (30%) provided benzophenone azine (35 mg, 7%) and recovered **1a** (30 mg). The bicyclic dione **5a** (91 mg, 12%) was eluted with hexane–benzene (50%). The **4a** (25 mg, 4%), **3a** (282 mg, 43%), and **2a** (252 mg, 30%) were yielded on further chromatographic treatment as above. Recrystallization of **5a** from a mixture of hexane and benzene yielded pale yellow needles: mp 173—174 °C; IR (KBr) 1666, 1493, 1302, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.33 (s, 2H, cyclopropyl H), 6.18 (s, 2H, vinyl H), 7.2—7.6 (m, 10H, aromatic H); MS, *m/z* 274 (M^+). Anal. ($C_{19}H_{14}O_2$) C, H.

5- or 6-Chloro-4,7-dihydroxy-3,3-diphenyl-3*H*-indazole (2b or 2b') and 7-Benzhydryloxy-5- or 6-chloro-4-hydroxy-3,3-diphenyl-3*H*-indazole (3b or 3b'). A benzene solution (20 ml) of DDM (700 mg, 3.61 mmol) and 2-chloro-1,4-benzoquinone **1b** (515 mg, 3.61 mmol) was allowed to stand for 10 h at 25 °C. The solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (20 to 100%) gave successively benzophenone **6** (35 mg, 5%), recovered **1b** (100 mg), **3b** (248 mg, 27%), and **3b'** (265 mg, 29%). Further elution with benzene–ether (5%) yielded **2b'** (210 mg, 17%) and **2b** (85 mg, 7%). The **2b** and **2b'** were converted into **3b** and **3b'** respectively, when treated with DDM. Recrystallization of **2b** from benzene provided yellow crystals: mp 180 °C (decomp); IR (KBr) 3473, 1460, 1401, 1242, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.05 (broad s, 1H, OH, exchangeable with CD_3OD), 5.50 (broad s, 1H, OH, exchangeable with CD_3OD), 7.1—7.4 (m, 11H, aromatic H); MS *m/z* 336 (M^+). Anal. ($C_{19}H_{13}O_2N_2Cl$) C, H, N. Recrystallization of **2b'** from benzene gave yellow crystals: mp 172—174 °C; IR (KBr) 3398, 1493, 1452, 1228, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.83 (broad s, 1H, OH, exchangeable with CD_3OD), 5.40 (broad s, 1H, OH, exchangeable with CD_3OD), 7.2—7.4 (m, 11H, aromatic H); MS, *m/z* 336 (M^+). Anal. ($C_{19}H_{13}O_2N_2Cl$) C, H, N. Recrystallization of **3b** from a mixture of hexane and benzene provided yellow crystals of mp 86—88 °C; IR (KBr) 3429, 1480, 1460, 1230, 1040, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.33 (s, 1H, OH, exchangeable with CD_3OD), 7.00 (s, 1H, $Ph_2C\underline{H}$), 7.1—7.7 (m, 21H, aromatic H); MS, *m/z* 502 (M^+). Anal. ($C_{32}H_{23}O_2N_2Cl$) C, H, N. Recrystallization of **3b'** from benzene yielded yellow crystals which decomposed at 178 °C (decomp); IR (KBr) 3429, 1491, 1460, 1240, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.77 (s, 1H, OH, exchangeable with CD_3OD), 6.87 (s, 1H, $Ph_2C\underline{H}$), 6.9—7.8 (m, 21H, aromatic H); MS, *m/z* 502 (M^+). Anal. ($C_{32}H_{23}O_2N_2Cl$) C, H, N.

3-Chloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (5b). To a refluxing benzene (10 ml) containing **1b** (515 mg, 3.61 mmol) was added dropwise over 10 min a benzene solution (10 ml) of DDM (700 mg, 3.61 mmol). After 1 h refluxing, the solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (20—50%) gave successively **6** (40 mg, 6%), recovered **1b** (90 mg), and benzophenone azine (25 mg, 4%). The bicyclic dione **5b** (171 mg, 15%) was eluted with hexane–benzene (50%) and recrystallized from a mixture of hexane and benzene to yield pale yellow prisms: mp 104—105 °C; IR (KBr) 1684, 1661, 1595, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.2—3.3 (m, 2H, cyclopropyl H), 6.33 (d, *J*=1.5 Hz, 1H, vinyl H), 7.0—7.3 (m, 10H, aromatic H); MS, *m/z* 308 (M^+). Anal. ($C_{19}H_{13}O_2Cl$) C, H. The **3b** (205 mg, 23%), **3b'** (230 mg, 25%), **2b'** (125 mg, 10%), and **2b** (63 mg, 5%) were obtained on further column-chromatographic treatment as above.

5,6-Dichloro-4,7-dihydroxy-3,3-diphenyl-3*H*-indazole (2c) and 7-Benzhydryloxy-5,6-dichloro-4-hydroxy-3,3-diphenyl-3*H*-indazole (3c). A benzene solution (10 ml) of DDM (290 mg, 1.49 mmol) and 2,3-dichloro-1,4-benzoquinone **1c** (260 mg, 1.47 mmol) was allowed to stand for 10 h at 25 °C. The solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (30 to 100%) gave successively **6** (35 mg, 13%), recovered **1c** (120 mg), and **3c** (240 mg, 60%). Further elution with benzene–ether (5%) yielded 2,3-dichlorohydroquinone (13 mg, 5%) and **2c** (93 mg, 17%). Recrystallization of **2c** from a mixture of hexane and ether provided yellow glanulates: mp 173—174 °C; IR (KBr) 3427, 1451, 1099, 696 cm^{-1}; ^1H NMR (acetone-d_6) δ=2.9 (broad s, 1H, OH, exchangeable with CD_3OD), 7.30 (s, 10H, aromatic H), 8.30 (broad s, 1H, OH, exchangeable with CD_3OD); MS, *m/z* 370 (M^+). Anal. ($C_{19}H_{12}O_2N_2Cl_2$) C, H, N. Recrystallization of **3c** from a mixture of hexane and benzene provided pale yellow crystals: mp 166—168 °C; IR (KBr) 3431, 1438, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.48 (s, 1H, OH, exchangeable with CD_3OD), 7.0—7.7 (m, 20H, aromatic H), 7.80 (s, 1H, $Ph_2C\underline{H}$); MS, *m/z* 536 (M^+). Anal. ($C_{32}H_{22}O_2N_2Cl$) C, H, N.

3,4-Dichloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (5c). To a refluxing benzene (5 ml) containing **1c** (260 mg, 1.47 mmol) was added dropwisely over 10 min a benzene solution (5 ml) of DDM (290 mg, 1.49 mmol). After 1 h refluxing, the solvent was removed and the residue was column-chromatographed on silica gel. Elution with hexane–benzene (30%) gave successively **6** (30 mg, 11%), recovered **1c** (75 mg), and bicyclic dione **5c** (25 mg, 5%). Recrystallization from benzene yielded pale yellow prisms: mp 237—238 °C; IR (KBr) 1691, 1561, 1277, 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.38 (s, 2H, cyclopropyl H), 7.2—7.5 (m, 10H, aromatic H); MS, *m/z* 343 (M^+). Anal. ($C_{19}H_{12}O_2Cl_2$) C, H. The **3c** (212 mg, 53%), 2,3-dichlorohydroquinone (15 mg, 6%), and **2c** (125 mg, 23%) were obtained on further column-chromatographic treatment as above.

1,3-Dichloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (5e), 1,3-Dichloro-4,4,8,8-tetraphenyltricyclo[5.1.0.$0^{3,5}$]-octane-2,6-dione (7e), and Benzophenone Dimethyl Acetal (9). A benzene solution (10 ml) of DDM (350 mg, 1.80 mmol), 2,6-dichloro-1,4-benzoquinone **1e** (320 mg, 1.81 mmol), and 5 equiv of methanol (300 mg) was allowed to stand for 15 h at 25 °C. The solvent was removed and the pasty residue was immediately submitted for ^1H NMR measurement. The absolute yields of bicyclic dione **5e** (43%), tricyclic dione **7e** (5%), and benzophenone dimethyl acetal **9** (45%) were determined by the integral ratios with 1,1,1,2-tetrachloroethane (δ=4.20) as an internal standard. Extraction with pentane (5 ml×3) left solid residue. Combined pentane extracts were column-chromatographed on alumina to yield acetal **9** (83 mg, 20%) and hydrolyzed **6** (60 mg, 18%) with hexane–benzene (20%). The structure of **9** was confirmed by comparison of the IR and NMR spectra with those of authentic sample. The solid residue was column-chromatographed on silica gel to give successively **7e** (49 mg, 5%) and **5e** (235 mg, 38%) with hexane–benzene (50%), and 2,6-dichlorohydroquinone (135 mg, 42%) with benzene–ether (10%). Recrystallization of **5e** from a mixture of hexane and benzene gave pale yellow prisms: mp 149—151 °C; IR (KBr) 1706, 1671, 709 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.54 (d, *J*=1.8 Hz, 1H, cyclopropyl H), 6.45 (d, *J*=1.8 Hz, 1H, vinyl H), 7.1—7.6 (m, 10H, aromatic H); MS, *m/z* 342 (M^+). Anal. ($C_{19}H_{12}O_2Cl_2$) C, H. Recrystallization of **7e** from a mixture of hexane and benzene yielded pale yellow prisms: mp 285 °C (decomp); IR (KBr) 1710, 1693, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.66 (s, 2H, cyclopropyl H), 7.2—7.4 (m, 20H, aromatic H); MS, *m/z* 508 (M^+). Anal. ($C_{32}H_{22}O_2Cl_2$) C, H.

1,3,4-Trichloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (5f). A benzene solution (10 ml) of DDM (440 mg, 2.27 mmol), 2,3,5-trichloro-1,4-benzoquinone **1f** (480 mg, 2.27 mmol), and 5 equiv of methanol (360 mg) was allowed to stand for 15 h at 25 °C. The solvent was removed and the pasty residue was submitted for ^1H NMR measurement to determine the absolute yields of bicyclic dione **5f** (37%) and **9** (55%). After complete hydrolysis of **9** by adding few drops of dilute hydrochloric acid, the reaction products were column-chromatographed on silica gel. Elution gave successively **6** (195 mg, 47%) and **5f** (290 mg, 34%) with hexane–benzene (30%), and 2,3,5-trichlorohydroquinone (265 mg, 55%) with benzene–ether (20%). Recrystallization of **5f** from a mixture of hexane–benzene yielded pale yellow prisms: mp 189—190 °C; IR (KBr) 1698, 1257, 1103, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.73 (s, 1H, cyclopropyl H), 7.0—7.5 (m, 10H, aromatic H); MS, *m/z* 376 (M^+). Anal. ($C_{19}H_{11}O_2Cl_3$) C, H.

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