# Addition of 9-Diazofluorene to Unsubstituted and Chloro-Substituted 1,4-Benzoquinones. A Comparison with the Addition of Diphenyldiazomethane

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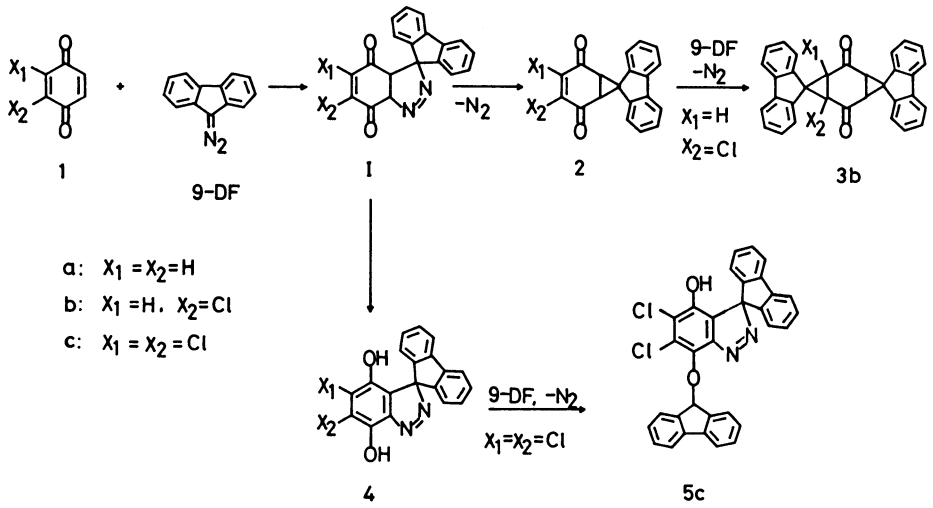
Unsubstituted 1,4-benzoquinone (**1a**) reacted at the C=C double bond with 9-diazofluorene (9-DF) to give norcarene dione **2a** and 4,7-dihydroxy-3*H*-indazole **4a**. Similarly, the reaction of 2-chloro-1,4-benzoquinone (**1b**) with 9-DF yielded norcarene dione **2b** and 4,7-dihydroxy-3*H*-indazole **4b**, together with tricyclic dione **3b**. 2,3-dichloro-1,4-benzoquinone (**1c**) and 9-DF produced norcarene dione **2c**, 4,7-dihydroxy-3*H*-indazole **4c**, and its fluorenyl ether **5c**. Reactions of 2,5- and 2,6-dichloro- and trichloro-1,4-benzoquinones (**1d**, **1e**, and **1f**) with 9-DF provided norcarene diones **2d**, **2e**, and **2f** and tricyclic diones **3d** and **3e**, respectively. On the other hand, tetrachloro-1,4-benzoquinone (**1g**) converted 9-DF into 9,9′-bifluorenylidene possibly via a 1 : 1 betaine intermediate arising from the C=O double bond addition. These results were markedly different from those of the previous diphenyldiazomethane reactions and are discussed in terms of structural changes of these diazoalkanes.

Since the early pioneering work by Pechmann for the addition of diazomethane to 1,4-benzoquinone,[1] the addition chemistry of diazoalkanes to quinones has received the continuing interest of several workers from synthetic and mechanistic points of view.[2] The products of these reactions are strongly dependent on the electronic and structural natures of these substrates. We previously reported that the reactions of diphenyldiazomethane (DDM) with unsubstituted and variously chloro-substituted 1,4-benzoquinones proceed through the addition to the quinonoid C=C or C=O double bonds, giving 4,7-dihydroxy-3*H*-indazoles, cyclopropane derivatives, or 1 : 1 betaine intermediates.[3] The addition modes varied with the numbers and with the substitution patterns of the chloro substituents. The unsubstituted quinone reacted only at the C=C double bond,[4] while the chlorinated quinones successively raised the proportion of the C=O addition with the increasing Cl substituents.[3] An extreme example is tetrachloro-1,4-benzoquinone, which reacted only at the C=O double bond.[5] We now report on an extended investigation of the reaction of planar 9-diazofluorene (9-DF) with a series of chloro-substituted 1,4-benzoquinones, especially focusing attention on the effects of the structural change of the diazoalkanes on the modes of additions.

## Results and Discussion

In 1955, Horner and Lingnau reported that the reaction of 9-DF with 1,4-benzoquinone (**1a**) gives 90% 4,7-dihydroxy-3*H*-indazole **4a** on standing for a long time, together with a small amount of nitrogen-free norcarene dione **2a** (2%).[6] About twenty years later, Shechter et al. attained a high yield (73%) of **2a** when the reaction was carried out in refluxing benzene.[7] These products appear to be given by way of dipolar addition, followed by two competitive processes; dienolization and nitrogen release of the primary adduct pyrazoline **I** (Scheme 1.)



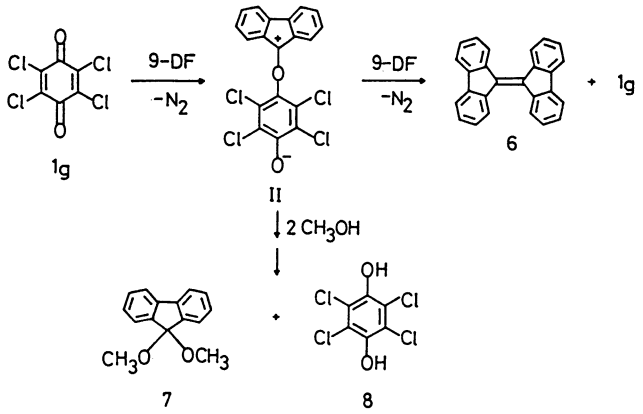

Scheme 1.

In contrast to Horner's result, but close to that of Shechter, the present equimolar reaction of 9-DF and **1a** yielded **2a** (61%) as a major product, even at 25 °C along with a moderate amount of **4a** (34%). An elevation of the reaction temperature to 60 °C moved the competing processes to the nitrogen release, as found in the yields of **2a** (77%) and **4a** (20%). A similar trend of accerelating the nitrogen release has been noticed for the previous reaction of diphenyldiazomethane (DDM) with **1a**.[3] The DDM reaction, which exclusively produced several dienolization products at 25 °C, gave rise to the corresponding norcarene dione in 12% yield at 80 °C.

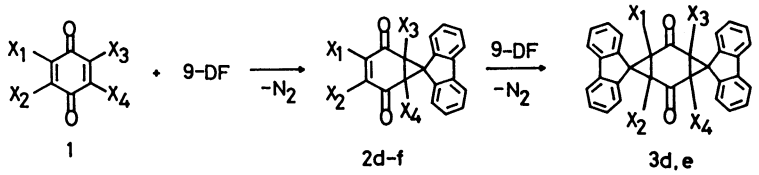
The reaction of 2-chloro-1,4-benzoquinone (**1b**) with 9-DF at 25 °C gave tricyclic dione **3b** (13%), together with norcarene dione **2b** (50%) and 4,7-dihydroxy-3*H*-indazole **4b** (22%). The diadduct **3b** is the secondary product arising from a further additon of 9-DF to the resulting **2b**, as confirmed by a treatment of 9-DF with **2b**. The stereochemistry of **3b** is unknown, partly because of the very low solubility in common solvents. However, **3b** was shown to be not a mixture of stereoisomers by a careful HPLC measurement. We tentatively assign the stereochemically pure **3b** to be the anti-form since the syn-configuration suffers a considerable steric repulsion between the fluorenylidene ring protons, as estimated from its molecular model.[8] The monoadduct **2b** offered coupled NMR peaks with a narrow range of $\delta$ 3.4—3.5 assignable to the two nonequivalent bridgehead protons in bicyclo[4.1.0]hept-3-ene-2,5-dione system, indicating that the addition took place at the unchlorinated C=C bond of **1b**. Evidently, this site selectivity may be ascribed to the steric repulsive effects exerted by the Cl substituent, because the MNDO calculation[9] rather predicts an opposite addition to the chlorinated C=C bond, as previously described in the case of DDM reactions.[3]

2,3-Dichloro-1,4-benzoquinone (**1c**) also reacted at the unchlorinated C=C bond and brought about a significant increase in dienolization products, **4c** (56%) and **5c** (10%), relative to norcarene dione **2c** (18%). This appears to be performed by the two meta- and para-directing Cl (electron-withdrawing) substituents, cooperatively capable of activating the migrating protons. The formation of fluorenyl ether **5c** of **4c** only for this case is also attributable to the two chloro substituents which increse the acidity of phenolic OH of **4c** to react with 9-DF. Such etherification was quite usual in the DDM reactions, where considerable amounts of benzhydryl ethers of the corresponding 4,7-dihydroxy-3*H*-indazoles were provided not only for **1c** but also for unchlorinated **1a** and monochlorinated **1b**.[3] Primarily, the lower nucleophilicity of 9-DF compared to DDM may be due to the conjugation between the diazo and planar dibenzocyclopentadienylidene moieties.[10]

Escaping dienolization owing to the lack of the unsubstituted C=C bonds, 2,5- and 2,6-dichloro-1,4-benzoquinones (**1d** and **1e**), and trichloro-1,4-benzoquinone (**1f**) gave norcarene diones, **2d** (80%), **2e** (10%), and **2f** (97%) and tricyclic diones, **3d**(8%) and **3e** (42%), respectively (Scheme 2). Compounds **3d** and **3e** seem to have a stable anti-form in analogy with **3b**. Rather surprising is the abnormally high yield of secondary product **3e** for the case of *m*-dichlorinated **1e**. This implies that the resulting **2e** tends to react with 9-DF much faster than does the parent quinone **1e**. Indeed, the second-order rate constant ($k$= $7.00\times10^{-3}$/s$^{-1}$ mol$^{-1}$, 30 °C, in benzene) of the addition of 9-DF to **2e** was about 5-times larger than that of the addition to **1e** ($1.31\times10^{-3}$). The intriguing behavior of **1e** was also noted for the DDM reactions, where only this quinone yielded a small amount of tricyclic dione in the ordinary conditions.[3] No explanation for these unusual results can be offered at the present




Scheme 3.




d: $X_1=X_4=Cl$, $X_2=X_3=H$
e: $X_1=X_3=Cl$, $X_2=X_4=H$
f: $X_1=X_2=X_3=Cl$, $X_4=H$

Scheme 2.

time.

As expected from the complete blocking of both of the C=C double bonds with the Cl substituents, tetrachloro-1,4-benzoquinone (**1g**) gave no norcarene dione with 9-DF as well as the reaction with DDM[5] but, rather, very slowly converted it into 9,9′-bifluorenylidene (**6**) at 25 °C.[10] However, refluxing an equimolar solution of 9-DF and **1g** in benzene ($1.30\times10^{-2}$ mol dm$^{-3}$) for ten hours provided an almost quantitative yield of **6** with a substantial recovery of **1g** (Scheme 3). This observation, combined with the fact that only 16% 9-DF underwent spontaneous decomposition to give **6** in an identical refluxing time (by HPLC), substantiates some certain participation of quinone **1g**, even in this accelerated condition. The formation of the dimeric olefin is suggestive of a carbenic process involving fluorenylidene (Fl).[11] An attempt was made to capture the possible carbene intermediate by adding 10 equiv excess of methanol. This trapping experiment at 80 °C still provided **6** in 90% yield, together with a small amount of fluorenone dimethyl acetal (**7**, 7%) and tetrachlorohydroquinone (**8**, 5%). The **7** and **8** can be regarded as arising from a redoxical acetalization of a 1 : 1 betaine intermediate II by considering that the reaction of DDM with **1g**[5] and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[12] proceeds through similar intermediates and affords benzophenone dimethyl acetal in high yield when methanol is introduced. However, the absence of fluorenyl methyl ether, a well-known methanol adduct with Fl,[13] does not bear out the carbene mechanism for the formation of a large amount of **6**. Here, it should be remembered that **1g** converted phenyldiazomethane into stilbene by way of a 1 : 1 betaine intermediate, like II.[14] Moreover, a very recent investigation of the reaction of 9-DF with DDQ revealed that this system also provides a small amount of **6** along with the norcarene dione at ordinary temperature.[15] The mechanistic interpretation for the formation of **6** rests on the 1 : 1 betaine intermediate. Accordingly, we believe that the most plausible pathway providing **6** likewise involves the betaine **II** as a key intermediate, as formulated in Scheme 3. Incidentally, a marked difference in the chemical behavior between DDM and 9-DF betaines is noticiable. The DDM betaines derived from **1g** and DDQ tended to polymerize to poly(hydroquinone benzhydryl ether)s and were well-collapsed by the addition of methanol to benzophenone dimethyl acetal and hydroquinones.[5,12] On the other hand, the possible 9-DF betaines did not polymerize but, rather, underwent a further attack of another molecule of 9-DF to produce dimeric olefin **6**.

Thus, the present 9-DF reactions were apparently different from the previous DDM reactions in that the former diazoalkane exhibited only C=C additions, with one exception of the C=O addition for tetrachlorinated **1g**. However, the latter one significantly increased the C=O additions with increasing the Cl substituents of quinones as follows: **1a**, 0%; **1b**, 9%; **1c**, 12%; **1d**, 51%; **1e**, 50%; **1f**, 60%; **1g**, 100%.[3] To explain the outstanding difference, we suggest that the most important effect of replacing the twisted diphenyl groups with the planar biphenyl-2,2′-diyl one at the diazo-carbon is to change the structural properties of the diazoalkanes so that the 9-DF can more easily approach the intrinsically reactive C=C double bonds than DDM. That 9-DF reactions furnished diadducts in fair yields for quinones **1b**, **1d**, and **1e** also attributable to such structural framework of 9-DF by which the less-repulsive access to the C=C double bonds of the monoadducts will be achieved. The gradual variation of the DDM reactions to the C=O additions in going from **1a** to **1g**, therefore, may be rationalized as a result of avoiding the increasing steric repulsion caused when the nonplanar DDM approaches the C=C double bonds with increasing Cl substituents. These steric considerations may also well explain the change of the addition modes of 9-DF and DDM toward DDQ. 9-DF preponderantly added to the C=C double bond having the CN substituents to give norcarene dione,[15] while DDM provided no such cycloadduct but instead afforded the product due to the C=O addition[12] in a manner similar to the reaction with **1g**.[5] The present 9-DF reactions are also characterized by providing large amounts of nitrogen-released cycloadducts for quinones **1a—c** in contrast to the DDM reactions. This is partly because the fluorenylidene structure, which resonates with the cleaving C(3)-N(2) bond much better than the diphenylmethylene one, would facilitate the loss of nitrogen from the pyrazoline adducts (**I**).

## Experimental

The IR, NMR, and mass spectra were taken with a Perkin Elmer 983G, a Varian EM 390, a JEOL GSX 400, and a Hitachi RMU 6E spectrometers, respectively.

**Materials.** The 9-diazofluorene (9-DF) was prepared by the oxidation of 9-fluorenone hydrazone with yellow mercury oxide[16] in ether and purified by recrystallization from ether; mp 94—95 °C. All quinones were provided and purified as described elsewhere.[3] Benzene was refluxed over lithium aluminium hydride and fractionated.

**Spiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2a) and Spiro[3*H*-indazole-3,9′-fluorene]-4,7-diol (4a).** A solution of **1a** (250 mg, 2.31 mmol) and 9-DF (444 mg, 2.31 mmol) in benzene (5 ml) was stored for 6 h at 25 °C. The precipitate was filtered, washed with ether (10 ml×2), and then with acetone (10 ml×2) to give analytically pure **2a** (305 mg, 48.5%). Recrystallization from a large volume of benzene yielded yellow needles: mp 256—257 °C, (lit,[6] 256 °C; lit,[7] 263—264 °C); IR(KBr) 1666, 1447, 734 cm$^{-1}$; $^1$H NMR($CDCl_3$) $\delta$=3.33 (s, 2H, cyclopropyl H), 6.8—7.9 (m, 10H, vinyl H+aromatic H); MS, *m/z* 272($M^+$). Anal. ($C_{19}H_{12}O_2$) C, H. The filtrate and the washing were combined and concentrated to dryness. The solid residue was chromatographed on silica gel to provide a second crop of **2a** (75 mg, 12%) with benzene as an eluent. Further elution

with benzene-ether (1 : 1) gave **4a** (235 mg, 34%); yellow crystals (from acetone), mp 250 °C (decomp) (lit,[6] 252 °C); IR(KBr) 3416, 3238, 1447, 1275, 748 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$=6.5—8.0 (m, 10H, aromatic H), 7.65 (s, 1H, OH, exchangeable with $CD_3OD$), 9.17 (s, 1H, OH, exchangeable with $CD_3OD$); MS, $m/z$ 300($M^+$). Anal. ($C_{19}H_{12}O_2N_2$) C, H, N.

In a separated experiment, equimolar **1a** (2.31 mmol) and 9-DF in benzene (5 ml) were allowed to react for 3 h at 60 °C. The **2a** (485 mg, 77%) and **4a** (140 mg, 20%) were obtained on the same work-up treatment as above.

**3′-Chlorospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2b), 1′-Chlorodispiro[fluorene-9,4′-tricyclo[5.1.0.0$^{3,5}$]octane-8′,9″-fluorene]-2′,6′-dione (3b), and 5-Chlorospiro[3*H*-indazole-3,9′-fluorene]-4,7-diol (4b).** A solution of **1b** (740 mg, 5.19 mmol) and 9-DF (1.00 g, 5.21 mmol) in benzene (15 ml) was allowed to stand for 6 h at 25 °C. The white solid formed was filtered and washed with acetone (10 ml×2) to give analytically pure **3b** (320 mg, 13%): mp 218—220 °C; IR(KBr) 1691, 1447, 1229, 734 $cm^{-1}$. The NMR of **3b** could not be determined because of its insolubility in common solvents. MS, $m/z$ 470 ($M^+$). Anal.($C_{32}H_{19}O_2Cl$) C, H. The filtrate and the washing were combined and evaporated to dryness. The solid residue was chromatographed on silica gel. Elution with hexane-benzene (1 : 3) yielded the recovered **1b** (90 mg). Further elution produced **2b** (795 mg, 50%) with benzene and **4b** (88 mg, 5%) with benzene-ether (1 : 1). Recrystallization of **2b** from benzene gave yellow prisms: mp 210—220 °C; IR(KBr) 1685, 1665, 736 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=3.43 (d×d, $J$=7.3 and 1.5 Hz, 1H, cyclopropyl H), 3.49 (d, $J$=7.3 Hz, 1H, cyclopropyl H), 6.9—7.9 (m, 9H, vinyl H+aromatic H); MS, $m/z$ 306 ($M^+$). Anal.($C_{19}H_{11}O_2Cl$) C, H. Recrystallization of **4b** from benzene-ether mixture provided yellow plates: mp 210 °C (decomp); IR(KBr) 3264, 1446, 1226, 750 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=4.83 (s, 1H, OH, exchangeable with $CD_3OD$), 6.6—7.9 (m, 9H, aromatic H), 8.00 (s, 1H, OH, exchangeable with $CD_3OD$); MS, $m/z$ 334 ($M^+$). Anal.($C_{19}H_{11}O_2N_2Cl$) C, H, N.

In a separate experiment, monoadduct **2b** (31 mg, 0.1 mmol) in benzene (1 ml) was allowed to react with excess 9-DF (96 mg, 0.5 mmol) for 1 d at 25 °C. Diadduct **3b** was obtained in 90% yield.

**3′,4′-Dichlorospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2c), 5,6-Dichlorospiro[3*H*-indazole-3,9′-fluorene]-4,7-diol (4c), and 5,6-Dichloro-7-(9-fluorenyloxy)spiro[3*H*-indazole-3,9′-fluoren]-4-ol (5c).** A solution of **1c** (330 mg, 1.86 mmol) and 9-DF (360 mg, 1.88 mmol) in benzene (5 ml) was stored for 3 h at 25 °C. The solvent was evaporated and the solid residue was chromatographed on silica gel. Elution with hexane-benzene (2 : 1) provided the recovered **1c** (30 mg) and **2c** (111 mg, 18%): mp 209—210 °C, yellow plates (from benzene); IR(KBr) 1687, 1555, 1079, 739 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=3.55 (s, 2H, cyclopropyl H), 6.8—7.8 (m, 8H, aromatic H); MS, $m/z$ 340 ($M^+$). Anal. ($C_{19}H_{10}O_2Cl_2$) C, H. Further elution with benzene gave **5c** (103 mg, 10%): mp 200 °C (decomp), pale yellow prisms (from chloroform); IR(KBr) 3437, 1435, 1197, 739 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=5.13 (s, 1H, OH, exchangeable with $CD_3OD$), 6.7—8.0 (m, 17H, methine+aromatic H); MS, $m/z$ 532 ($M^+$). Anal. ($C_{32}H_{18}O_2N_2Cl_2$) C, H, N. Finally, **4c** (386 mg, 56%) was eluted with benzene-ether (3 : 1). Recrystallization of **4c** from hexane-ether mixture yielded yellow needles: mp 215 °C (decomp); IR(KBr) 3424, 1449, 1083, 750 $cm^{-1}$; $^1H$ NMR(acetone-$d_6$) $\delta$=6.6—8.0 (m, 8H, aromatic H), 7.87 (s, 1H, OH, exchangeable with $CD_3OD$), 10.1 (s, 1H, OH, exchangeable with $CD_3OD$); MS, $m/z$ 368 ($M^+$). Anal. ($C_{19}H_{10}O_2N_2Cl_2$) C, H, N.

**1′,4′-Dichlorospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2d) and 1′,4′-Dichlorodispiro[fluorene-9,4′-tricyclo-[5.1.0.0$^{3,5}$]octane-8′,9″-fluorene]-2′,6′-dione (3d).** A solution of **1d** (660 mg, 3.73 mmol) and 9-DF (720 mg, 3.75 mmol) in benzene (20 ml) was stored for 1 d at 25 °C. The solid formed was filtered and washed with benzene (5 ml×2) to leave analytically pure **3d** (154 mg, 8%): mp>350 °C; IR(KBr) 1698, 1443, 1286, 736 $cm^{-1}$. The NMR of **3d** could not be taken because of its insolubitity. MS, $m/z$ 504 ($M^+$). Anal. ($C_{32}H_{18}O_2Cl_2$) C, H. The filtrate and the washing were combined and concentrated to give yellow crystals of **2d** (990 mg, 78%): mp 126—127 °C, pale yellow prisms (from benzene); IR(KBr) 1681, 1579, 989, 729 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=3.77 (s, 1H, cyclopropyl H), 7.19 (s, 1H, vinyl H), 7.1—7.9 (m, 8H, aromatic H); MS, $m/z$ 340 ($M^+$). Anal. ($C_{19}H_{10}O_2Cl_2$) C, H.

**1′,3′-Dichlorospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2e) and 1′,3′-Dichlorospiro[fluorene-9,4′-tricyclo-[5.1.0.0$^{3,5}$]octane-8′,9″-fluorene]-2′,6′-dione (3e).** A solution of **1e** (1.00 g, 5.65 mmol) and 9-DF (1.08 g, 5.62 mmol) in benzene (20 ml) was stored for 6 h at 25 °C. The solid formed was filtered and washed with benzene (5 ml×2) and acetone (5 ml×2) to leave analytically pure **3e** (1.20 g, 42%) as a pale-yellow powder: mp>350 °C; IR(KBr) 1711, 1448, 1216, 741 $cm^{-1}$. The NMR of **3e** could not be taken because of its insolubility. MS, $m/z$ 504($M^+$). Anal. ($C_{32}H_{18}O_2Cl_2$) C, H. The filtrate and the washing were concentrated and chromatographed on silica gel. After elution of the recovered **1d** (0.39 g) with hexane-benzene (2 : 1), the **2e** (245 mg, 13%) was obtained with benzene. Recrystallization with hexane-benzene mixture produced yellow prisms: mp 127—129 °C IR(KBr) 1699, 1666, 1589, 1263, 1058, 721 $cm^{-1}$; $^1H$ NMR($CDCl_3$) $\delta$=3.67(d, $J$=1.50 Hz, 1H, cyclopropyl H), 7.0—7.8 (m, 9H, vinyl H+aromatic H); MS, $m/z$ 340 ($M^+$). Anal. ($C_{19}H_{10}O_2Cl_2$) C, H.

In separate experiments, solutions of **1e** (300 mg, 1.69 mmol) and 9-DF (650 mg, 3.38 mmol) in benzene (5ml) and of **2e**(100 mg, 0.294 mmol) and 9-DF (57 mg, 0.297 mmol) in benzene (3ml) were allowed to react as above. Both reactions provided 1 : 2 adduct **3e** in more than 96% yield.

The kinetic reactions were carried out in the presence of 30- (for **1e**) and 12-fold (for **2e**) molar excess of 9-DF ($3.6—7.7\times10^{-2}$ mol $dm^{-3}$) to permit a pseudo-first-order kinetic treatment. The rates were determined by following the relative decrease of **1e** and **2e** with respect to *p*-cyanobenzaldehyde and solvent benzene as internal standards, respectively, with a Hitachi 655A-12 HPLC instrument equipped with a Hitachi D-2000 chromato-integrator. The HPLC conditions using a Radial Pak cartridge C18(Waters Associates, Inc.) are as follows; 1 ml $min^{-1}$, eluents: 30% (for **1e**) and 20% aqueous methanol (v/v) (for **2e**), UV-detector wavelength: 254 and 273 nm for **1e** and **2e**, respectively.

**1′,3′,4′-Trichlorospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (2f).** A solution of **1f** (600 mg, 2.84 mmol) and 9-DF (545 mg, 2.84 mmol) in benzene (10 ml) was stored at 25 °C for 3 d. The solid formed was filtered and washed with benzene (5 ml×3) to give **2f** (980 mg, 92%): mp 210 °C (decomp), orange granulates (from acetone); IR(KBr) 1692,

1225, 1088, 729 $cm^{-1}$; $^1H$ NMR(acetone-$d_6$) $\delta$=4.18 (s, 1H, cyclopropyl H), 6.7—7.8(m, 8H, aromatic H); MS, *m/z* 374 ($M^+$). Anal. ($C_{19}H_9O_2Cl_3$) C, H. The filtrate was chromatographed on silica gel to yield a second crop of **2f** (53 mg, 5%) with benzene as an eluent.

**Reaction of 9-DF with Tetrachloro-1,4-benzoquione (1g) with or without Added Methanol.** A solution of 9-DF (0.50 g, 2.6 mmol) and **1g** (0.64 g, 2.6 mmol) in benzene (20 ml) was refluxed for 10 h. The solvent was evaporated and the dark-red residue was washed with ether (10 ml×3) to give recovered **1g** (0.45 g, 70%). The ether solution was concentrated to dryness and subjected to silica-gel chromatography. Elution with hexane-benzene (1:4 v/v) yielded 9,9′-bifluorenylidene (**6**, 415 mg, 97%) and the second crop of **1g** (0.18 g, 28%).

As a trapping experiment, a solution of 9-DF (0.50 g), **1g** (0.64 g), and 10 equiv of methanol (0.83 g) in benzene (20 ml) was refluxed for 10 h. The same work-up as above recovered **1g** (0.40 g, 62.5%). The washing ether was evaporated and the dark-red residue was immediately submitted for NMR measurement. The singlet at $\delta$ 3.30 ($CDCl_3$), which was only one signal detectable in a field higher than $\delta$ 7.0 was assigned to the $CH_3O$ groups of fluorenone dimethyl acetal (**7**) by comparison with spectrum of authentic sample[17] as well as chemical proof being hydrolyzed to fluorenone upon treatment with dilute hydrochloric acid. The absolute yield of acetal **7** (7%) was determined by the integral ratio with 1,1,1,2-tetrachloroethane ($\delta$=4.20) as an internal standard. After a complete hydrolysis of acetal, the reaction product on chromatography over silica gel gave **6** (385 mg, 90%), the second crop of recovered **1g** (175 mg, 27%), and fluorenone (30 mg, 6%) with 5—30% benzene in hexane and tetrachlorohydroquinone (**8**, 30 mg, 5%) with 5% ether in benzene.

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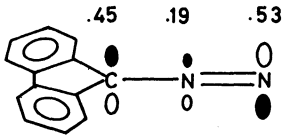


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