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Products and Kinetic Substituent Effects in the Reactions of Diaryldiazomethanes with 2,5-Dichloro-*p*-benzoquinone

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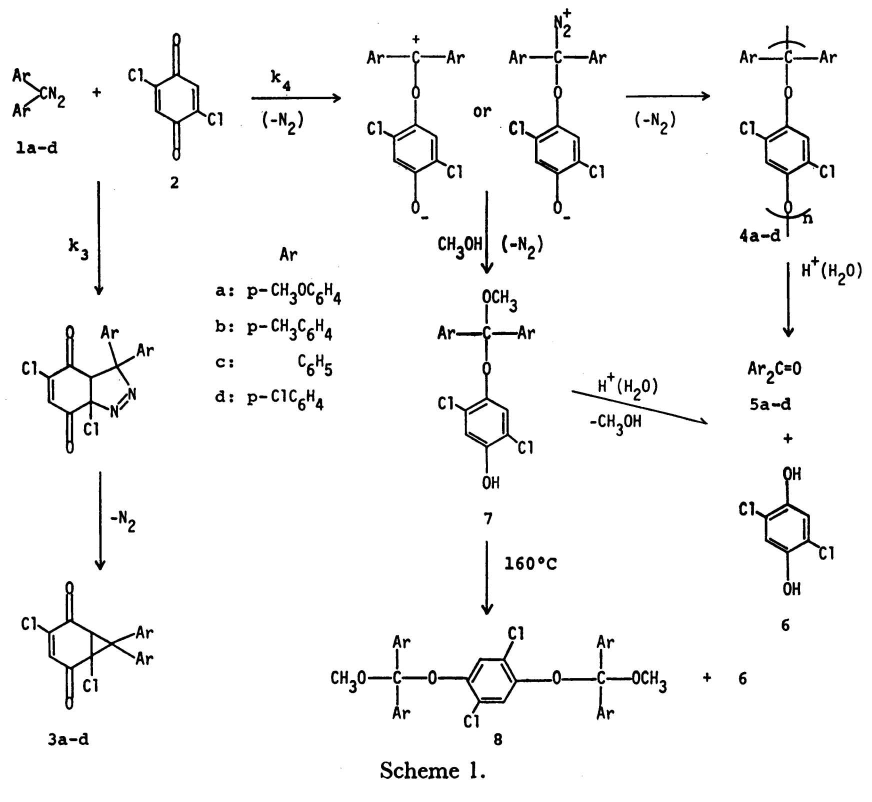
Substituted diphenyldiazomethanes[$(x\text{-}C_6H_4)_2CN_2$; x=*p*-OCH_3, *p*-CH_3, H, *p*-Cl] were found to react with 2,5-dichloro-*p*-benzoquinone at its conjugated C=C and C=O bonds to give bicyclic diones and poly(2,5-dichlorohydroquinone benzhydryl ether)s respectively, obeying the second-order kinetic law. The product ratios of the polyethers to the bicyclic diones increased from 1.1 to 8.1 with the electron-donating ability of the substituents. The individual rate constants were well correlated with the Hammett equation: $\log k_3 = -2.15 - 1.55\,\sigma$ ($r=0.996$) and $\log k_4 = -2.03 - 1.85\,(\sigma^0 + 0.515\Delta\bar{\sigma}_R{}^+)$ ($r=1.00$) for the bicyclic diones and polyethers processes respectively. The presence of methanol as a trapping agent stopped the polymerization completely and afforded the methanolysis product, though no essential change was found in the formation of the bicyclic dione.

In the reaction of diazomethane or diazoethane with 2,5-dichloro-*p*-benzoquinone (**2**), Eistert *et al.*[1] obtained pyrazoline derivatives formed *via* 2+3 cycloaddition toward the C=C bonds of the quinone. In contrast to **2**, tetrasubstituted quinones, such as chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), are known to react with diazomethane at the C=O bonds, giving oxirane derivatives.[2,3] Recently, we showed that these quinones also react at the C=O bonds with aryl- and diaryldiazomethanes to give stilbenes and spirooxetanes[4] and poly(hydroquinone benzhydryl ether)s[5,6] respectively. Thus, **2** differs from chloranil or DDQ in its reaction pattern toward the diazoalkanes. However, no reactions of **2** with diaryldiazomethanes have hitherto been known. Therefore, we have carried out the reactions of diaryldiazomethanes with **2** in order to obtain further insight into the factors governing the reaction mode and also in order to compare the results with those of chloranil and DDQ reactions.

We found that **2** reacts with diaryldiazomethanes at both the C=C and C=O bonds, yielding bicyclic diones and poly(2,5-dichlorohydroquinone benzhydryl ether)s. Kinetic substituent effects in these two reaction courses were also discussed.

Results and Discussion

Product Analysis. The reactions of disubstituted diaryldiazomethanes (**1a**—**d**) with an equimolar amount of 2,5-dichloro-*p*-benzoquinone (**2**) were carried out in 1,2-dichloroethane at 30 °C. The **1a** with the *p,p'*-OCH_3 substituents violently decomposed, with an evolution of N_2 and the immediate deposition of white precipitates, while the **1d** with the *p,p'*-Cl substituents needed *ca.* 10 h for the complete disappearance of the diazo color. All these reactions gave considerable amounts of white precipitates. The filtrate was evaporated to dryness, followed by column chromatography



Scheme 1.

on silica gel to give bicyclic diones (**3a**—**d**) (Scheme 1). The ^1H NMR spectra showed the vinylic proton at the lower fields (δ, 6.60—6.65) and the cyclopropyl proton at the higher fields (3.58—3.67), in accordance with the bicyclic structure. The precipitate isolated in the reaction of **1a** was gradually hydrolyzed into almost equimolar amounts of *p,p'*-dimethoxybenzophenone (**5a**) and 2,5-dichlorohydroquinone (**6**) during the work-up. However, the precipitates for **1b**—**d** were so stable that the complete hydrolyses needed refluxing for 8—20 h in aqueous methanol containing hydrochloric acid. These hydrolyses gave almost equimolar amounts of benzophenones (**5b**—**d**) and **6**. Next, we examined the effect of methanol as an additive on the reaction features employing **1c**. No essential change was found in the yield of **3c**, but a different product, 2,5-dichloro-4-[(methoxy)diphenylmethoxy]phenol (**7**), was provided instead of the precipitate. The **7** was easily hydrolyzed into **5c** and **6** under the influence of hydrochloric acid, whereas a short-time heating slightly over its melting point (151 °C) smoothly brought about the disproportionation to yield 2,5-dichloro-1,4-bis[(methoxy)-diphenylmethoxy]benzene (**8**) and **6**.

It can be suggested that the bicyclic diones (**3a**—**d**) may be produced *via* 1,3-dipolar cycloaddition, followed by the rapid elimination of N_2 from the resulting pyrazolines, considering that methanol does not participate as an additive. With regard to the structure of white precipitates, poly(2,5-dichlorohydroquinone benzhydryl ether)s (**4a**—**d**) are conceivable from the observations that the IR spectra of the stable precipitates for the **1b**—**d** showed no carbonyl, but strong absorptions assignable to the ethereal bonds, and also that the hydrolyses gave equimolecular amounts of benzophenones and **6**. In analogy with the reactions with chloranil[5] and DDQ,[6] the formation of polyethers prompted us to suggest the operation of the same mechanism in these polymerization reactions (Scheme 1). We had previously proposed the diazonium or carbonium betaine as the intermediate in chloranil and DDQ systems.[5,6] In fact, the presence of methanol as a trapping agent stopped the polymerization completely and afforded the methanolysis product, **7**, instead of the polyether, though the 2+3 cycloaddition process leading to **3c** was little affected.

The results are summarized in Table 1. The product ratios of **4** to **3** increased in the order of **1a**>**1b**>**1c**>**1d**, with the electron-donating ability of the substituents.

Table 2. Observed second-order rate constants, k_{obsd}, and the individual rate constants, k_3 and k_4, for the process giving **3** and **4** in the reactions of **1a**—**d** with **2** in CH_2ClCH_2Cl at 30°C

Compound	$10^3 k_{obsd}$ / $l\ mol^{-1}\ s^{-1}$	$10^3 k_3$[a] / $l\ mol^{-1}\ s^{-1}$	$10^3 k_4$[a] / $l\ mol^{-1}\ s^{-1}$
1a	463	51.0	412
1b	81.9	24.1	57.8
1c	14.9	5.81	9.09
1d	3.24	1.54	1.70

a) The values determined by multiplying k_{obsd} by the relative yields of **3** and **4**.

A comparison of the present results with those observed in the reaction with diazomethane[1] and in the diaryldiazomethanes–chloranil[5] and –DDQ systems[6] is of some interest from the mechanistic point of view. The **2** is known to react at the C=C bonds with two moles of diazomethane to produce the pyrazoline derivative,[1] while the C=O bonds of **2** are unreactive toward diazomethane. On the other hand, the diaryldiazomethanes can react at both the C=O and the C=C bonds of **2**. In contrast to the case of **2**, the 2+3 cycloaddition process is not anticipated in the reactions of diaryldiazomethanes with chloranil[5] and DDQ,[6] where the C=O bonds selectively participate in the reactions. The lack of such bicyclic diones in the chloranil and DDQ reactions is certainly attributable to the larger steric hindrance due to the bulky Cl and/or CN substituents on either side of the C=C bonds, by which the approach of diaryldiazomethanes (even diazomethane and aryldiazomethane) to the double bonds is inhibited.

It is also noticed that the polyethers derived from **2** are more stable against solvolyses than those derived from chloranil or DDQ. In addition, the presence of methanol in the chloranil or DDQ reaction inhibited the formation of polyether, as in the present case, but the initially resulting methanolysis products like **7** further underwent a nucleophilic attack by methanol to be converted into α,α-dimethoxydiphenylmethane and the respective hydroquinones.[5,6] These chemical observations are probably the result of the stronger electron-acceptor ability of chloranil and DDQ moieties than that of **2**;[7] hence, the ethereal C–O linkage for the chloranil or DDQ reaction is much more subject to hydrolysis and methanolysis than those for the **2** reaction.

Kinetic Study. Substituent Effects: The 1,2-dichloroethane solutions of **1a**—**d** used for kinetic purposes were diluted by a factor of about 10 compared to those for the product study. Thus, the decompositions of **1a**—**d** at 30 °C could be followed spectrophotometrically over 60—70% reactions without the disturbance due to the suspension of polyethers (**4a**—**d**). The observed second-order rate constants increased with the electron-donating ability of the *p*-substituents (Table 2). From the results in Tables 1 and 2, one can easily obtain the

Table 1. Product distributions in the equimolar (5.67 mmol) reactions of diaryldiazomethanes (**1a**—**d**) and 2,5-dichloro-*p*-benzoquinone (**2**) in CH_2ClCH_2Cl at 30 °C

Compound	Additive	Reaction time / h	Yield/%[a] **3**	Yield/%[a] **4**	Yield/%[a] **7**
1a	—	1	10.5	85.1[c]	—
1b	—	1	28.0	67.3[c]	—
1c	—	2	38.1	59.7[c]	—
1c	CH_3OH[b]	2	37.6	—	58.6
1d	—	6	46.3	51.2[c]	—

a) Yield as mole percentage based on **1**. b) A five-fold molar excess was added with respect to **1c**. c) Based on the benzophenones (**5a**—**d**) obtained by the hydrolyses of **4a**—**d**.

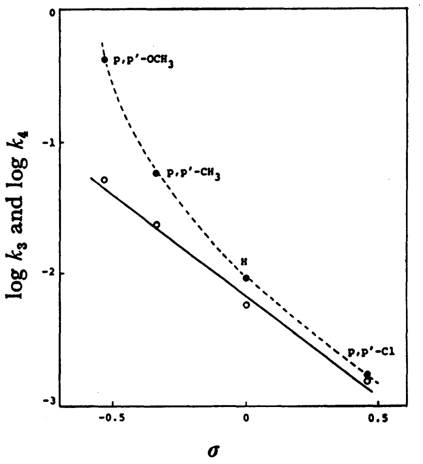


Fig. 1. The plots of log k_3 (○) and log k_4 (●) against the Hammett σ constants.

individual rate constants leading to the formations of **3a**—**d** and **4a**—**d** by multiplying the observed rate constants by the relative product ratios. The rate constants, k_3 and k_4, thus determined may also be seen in Table 2.

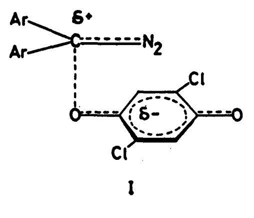
The dependence of the logarithmic rate constants on the Hammett σ constants[8] is shown in Fig. 1. As may easily be noticed, **3a**—**d** formation gave an excellent linear dependence (Eq. 1), where r, s, and n are the correlation coefficient, the standard deviation, and the data points respectively:

$$\log k_3 = -2.51 - 1.55\,\sigma$$
$$(r = 0.996,\ s = 0.0735,\ n = 4). \qquad (1)$$

However, the correlation line for the **4a**—**d** process displayed an upward deviation, especially in the OCH$_3$ substituent. The replacement of σ by the Brown σ^+ constants[9] was also unsuccessful, causing a downward deviation. Neither the σ nor σ^+ values apparently fit the correlation of the logarithmic rate constants for the **4a**—**d** process well. Therefore, we attempted the two-parameter Yukawa-Tsuno equation,[10] $\log k = \rho(\sigma^0 + R\Delta\bar{\sigma}_R^+)$, where σ^0, R, and $\Delta\bar{\sigma}_R^+$ are the normal substituent constants, the resonance reaction constant, and the resonance substituent constant respectively. The result of regression analysis indicates that the use of the two-parameter equation improves the correlation significantly (Eq. 2):

$$\log k_4 = -2.03 - 1.85\,(\sigma^0 + 0.515\,\Delta\bar{\sigma}_R^+)$$
$$(r = 1.00,\ s = 0.0105,\ n = 4). \qquad (2)$$

A comparison of the ρ values in Eqs. 1 and 2 shows a larger susceptibility of the rate of the **4a**—**d** process on the substituents than that of the **3a**—**d** process. Also, the value of R=0.515 confirms that a substantial π-resonance stabilization of a transition state operate in the **4a**—**d** process. By analogy to the mechanism of the reactions of diaryldiazomethanes with chloranil and DDQ, a similar transition state such as I is likely to account for the electronic demand. On the contrary, the process leading to **3a**—**d** may be through the 1,3-dipolar addition mechanism, since the rate constants were well correlated with the simple Hammett equation using normal σ values† in accordance with the product analysis, where no essential change was found in the yield of the bicyclic dione, as has been mentioned above.



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Experimental

The IR, NMR, and UV spectra were recorded on a Hitachi 215, a Varian EM-360, and a JASCO UVIDEC 505 spectrophotometer respectively.

Materials. The 2,5-dichloro-*p*-benzoquinone (**2**) was prepared according to the procedure described by A. R. Ling[12] and was recrystallized from ethanol; pale yellow prisms, mp 164—166 °C (lit, 161 °C).[12] The diaryldiazomethane were made by the oxidation of the corresponding hydrazones with yellow mercury(II) oxide, as has been described.[5] The physical properties of these diazoalkanes were listed in previous papers.[5,13] The 1,2-dichloroethane was dried over phosphorus pentaoxide and fractionated.

Kinetic Measurements. The values of k were determined spectrophotometrically by monitoring the decrease in the absorption of **1a**—**d** at the maximum wavelength (524—540 nm) in the visible region. The mean deviations were ±3% (usually two determinations). The temperature was kept at 30 °C (±0.1 °C) by means of a Haake circulator.

*Reactions of Diaryldiazomethanes (**1a**—**d**) with **2** in CH_2ClCH_2Cl.* The reaction of **1c** is described below as a typical example; the reactions of the other diazoalkanes were carried out similarly till the diazo color completely disappeared . To a stirred 1,2-dichloroethane solution (30 ml) of **2** (1.0 g, 5.65 mmol) was added, drop by drop, a 1,2-dichloroethane solution (10 ml) containing **1c** (1.1 g, 5.67 mmol) at 30 °C. A vigorous evolution of N$_2$ was observed except for the case of **1d**. After the mixture had been stirred for 2 h (1 h for **1a** and 6 h for **1d**), the white precipitate which appeared was filtered, washed with a small portion of 1,2-dichloroethane, and submitted to IR measurement. The precipitate in the case of **1a** was easily hydrolyzed into *p,p'*-dimethoxybenzophenone (**5a**) and **6** on the work-up. On the other hand, the precipitates in the cases of **1b**—**d** were stable enough to be hydrolyzed only in refluxing aqueous methanol containing hydrochloric acid for 8—20 h; they thus gave the corresponding benzophenones (**5b**—**d**) and **6**. The column chromatography (silica gel) of the hydrolyzed products gave an almost equimolar amount of **5a**—**d** (benzene as an eluent) and **6** (benzene–ether). These compounds were identified by a comparison of their IR spectra with those of authentic samples.[5,12] On the other hand, the filtrate parts were dried *in vacuo*, and the residues were chromatographed on silica gel. Elution with benzene gave pure bicyclic diones (**3a**—**d**). The structures of **3a**—**d** were identified by means of the IR, the NMR, and the elemental analyses.

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† The rate enhancement by the electron-donating substituents can be explained in terms of the increase in the HO-(dipole)-LU (dipolarophile) interaction in the concerted 1,3-dipolar addition by a raising of the HO energy.[11]

*1,4-Dichloro-7,7-bis(*p-*methoxyphenyl)bicyclo[4.1.0]hept-3-ene-2,5-dione (**3a**).* Pale yellow prisms (petroleum ether–benzene); mp 148—150 °C. IR (KBr): 3055, 1693, 1509, 1243 cm^{-1}. NMR (δ, $CDCl_3$): 3.62 (1H, s, cyclopropyl H), 3.73 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 6.56 (1H, s, vinyl H), 6.8—7.5 (8H, m, aromatic H). MS: *m/e* 402 (M^+). Found: C, 62.64; H, 4.05%. Calcd for $C_{21}H_{16}Cl_2O_4$: C, 62.54; H, 4.00%.

*1,4-Dichloro-7,7-di-*p-*tolylbicyclo[4.1.0]hept-3-ene-2,5-dione (**3b**).* Pale yellow prisms (ether); mp 151—153 °C. IR (KBr): 3053, 1684, 1588, 1512, 1291. 1063, 995, 820 cm^{-1}. NMR (δ, $CDCl_3$): 2.27 (3H, s, CH_3), 2.30 (3H, s, CH_3), 3.62 (1H, s, cyclopropyl H), 6.60 (1H, s, vinyl H), 7.03 (4H, s, aromatic H), 7.1—7.5 (4H, m, aromatic H). MS: *m/e* 370 (M^+). Found: C, 68.16; H, 4.41%. Calcd for $C_{21}H_{16}Cl_2O_2$: C, 67.94; H, 4.34%.

*1,4-Dichloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (**3c**).* Pale yellow prisms (petroleum ether–benzene); mp 179—180 °C. IR (KBr): 3052, 1703, 1689, 1597, 1295, 1062, 996, 709 cm^{-1}. NMR (δ, $CDCl_3$): 3.67 (1H, s, cyclopropyl H), 6.61 (1H, s, vinyl H), 7.0—7.6 (10H, m, aromatic H). MS: *m/e* 342 (M^+). Found: C, 66.71; H, 3.59%. Calcd for $C_{19}H_{12}Cl_2O_2$: C, 66.49; H, 3.53%.

*1,4-Dichloro-7,7-bis(*p-*chlorophenyl) bicyclo[4.1.0]hept-3-ene-2,5-dione (**3d**).* Pale yellow prisms (benzene); mp 209—210 °C. IR (KBr): 3051, 1701, 1677, 1584, 1485, 1087, 995, 833 cm^{-1}. NMR (δ, $CDCl_3$): 3.58 (1H, s, cyclopropyl H), 6.63 (1H, s, vinyl H), 7.1—7.3 (8H, m, aromatic H). MS: *m/e* 410 (M^+). Found: C, 55.58; H, 2.48%. Calcd for $C_{19}H_{10}Cl_4O_2$: C, 55.37; H, 2.45%.

*Reaction of **1c** with **2** in CH_3OH-CH_2ClCH_2Cl.* To a stirred 1,2-dichloroethane solution (30 ml) of **2** (1.0 g, 5.65 mmol) was added, drop by drop, a 1,2-dichloroethane solution (10 ml) containing **1c** (1.10 g, 5.67 mmol) and a 5-fold molar excess of methanol (0.9 g) at 30 °C. In contrast to the reactions in the absence of methanol, no precipitate was found. After having been stirred for 2 h, the solvent was evaporated and the trituration of the resinous products with 3×30 ml pentane left **3c** (0.72 g, 37%). The combined pentane solution was concentrated to afford 2,5-dichloro-4-[(methoxy)diphenylmethoxy]phenol (**7**); mp 151 °C (dec) IR (KBr): 3520, 1476, 1203, 1002 cm^{-1}, NMR (δ, $CDCl_3$): 3.30 (3H, s, OCH_3), 5.17 (1H, s, OH), 7.0—7.8 (12H, m, aromatic H), MS: *m/e* 343 ($M^+ - OCH_3$), Found: C, 64.03; H, 4.13%. Calcd for $C_{20}H_{16}Cl_2O_3$: C, 64.02; H, 4.26%. The **7** was easily hydrolyzed into benzophenone and **6** under the influence of aqueous methanol saturated with hydrochloric acid. When heated at 160 °C for 2 min, however, the **7** underwent a disproportionation into 2,5-dichloro-1,4-bis[(methoxy)diphenylmethoxy]benzene (**8**) and **6**. The **8** had a mp of 269—271 °C (from benzene); IR (KBr): 1477, 1211, 1091, 991, 697 cm^{-1}, NMR (δ, $CDCl_3$): 3.20 (6H, s, OCH_3), 7.0—7.7 (22H, m, aromatic H), MS: *m/e* 539 ($M^+ - OCH_3$), Found: C, 71.55; H, 4.97; Cl, 12.60%. Calcd for $C_{34}H_{28}Cl_2O_4$: C, 71.45; H, 4.94; Cl, 12.40%.

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