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Structural Effects in the Reactions of Diazoalkanes with 2,3-Dichloro-5,6-dicyanobenzoquinone

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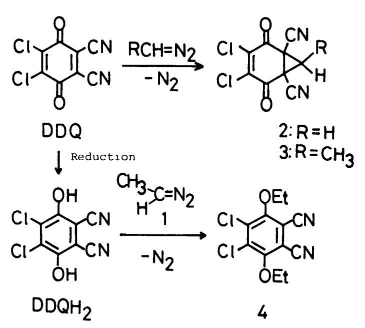
2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) reacted with diazoethane to give stereoisomeric bicyclic diones (**3**, isomer ratio=3.4) arising from dipolar addition to the C=C bond of DDQ. DDQ reacted with phenyldiazomethane to afford also stereoisomeric bicyclic diones (**7**) in the ratio of 5 : 1, together with stilbenes (**8**). On the other hand, DDQ gave the (ethenyloxy)benzene derivative (**14**) with 1-phenyldiazoethane. The formation of **8** and **14** was interpreted by considering the participation of 1 : 1 betaines resulting from addition to the C=O bond. The added methanol captures the betaines, thus giving rise to dimethyl acetals of benzaldehyde and acetophenone, along with 2,3-dichloro-5,6-dicyanohydroquinone. These reactivities of DDQ were discussed in comparison with those of chloranil.

As one area of the addition chemistry of quinones, comprehensive studies have been made of reactions with diazoalkanes from the synthetic and mechanistic points of view.[1] Quinones behave as dipolarophiles[2] as a result of their conjugated C=C and C=O bonds, while diazoalkanes behave as 1,3-dipoles.[3] A number of reports have been concerned with the reaction of diazomethane because of its commonness and high reactivity. Diazomethane tends to add to the conjugated C=C bonds of 1,4-benzoquinone[4] and its mono-, di-,[5] and trichlorinated analogues[6] to yield pyrazolines. On the other hand, the C=O bonds become active when the C=C bonds are blocked with the bulky halogens, as is exemplified in the formation of the oxirane derivative in the reaction with chloranil.[7] Recently, we extended the reaction of chloranil to phenyldiazomethane,[8] diphenyldiazomethane,[9] and 1-phenyldiazoethane,[10] and found that these diazoalkanes similarly add to the C=O bond, but variously provide stilbenes and spirooxetane, and poly(tetrachlorohydroquinone benzhydrylether), and 1-alkoxy-4-ethenyloxy-2,3,5,6-tetrachlorobenzene, respectively.

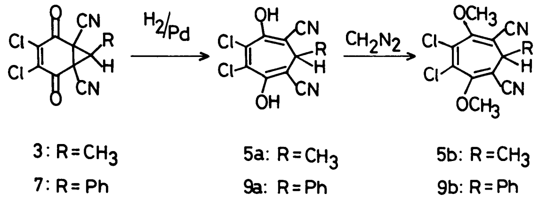
On the other hand, the reaction of diazomethane with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been reported to afford bicyclic dione (**2**),[11] in contrast to the reaction with chloranil. However, we found in a previous investigation[12] that DDQ reacts with diphenyldiazomethane in a manner similar to that of chloranil. In view of the general interest in the reactions of diazoalkanes with quinones, it is desirable to extend the DDQ reaction to other diazoalkanes of structural types not previously investigated. In this paper, reactions of DDQ with diazoethane, phenyldiazomethane, 1-phenyldiazoethane, were investigated in order to gain a better understanding of the structural effects on the reactivity of diazoalkanes and to compare the results with those obtained for the corresponding chloranil reactions.

Results and Discussion

Reaction with Diazoethane. Diazoethane (**1**) reacted with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to provide the bicyclic dione (**3**, isomer ratio=3.4), in analogy with diazomethane,[11,13] together with a small amount of 2,3-dichloro-5,6-dicyanohydroquinone diethyl ether (**4**) (Scheme 1). In conformity with the bicyclic dione structure, each isomer of **3** could be converted into the identical dimethoxycycloheptatriene derivative (**5b**) upon catalytic hydrogenation and the subsequent methylation (Scheme 2).



Scheme 1.



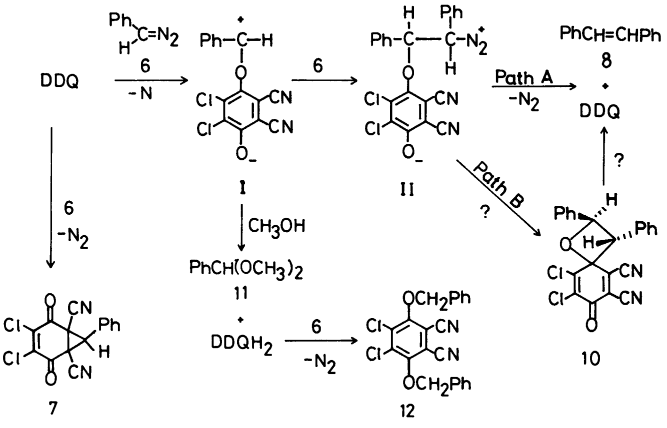
Scheme 2.

Though the ^{1}H NMR spectrum of the major isomer of **3** showed the methyl and cyclopropyl protons at a slightly higher field (0.1—0.2 ppm) than those of the minor one, it is not clear which of the two isomers corresponds to the exo or endo adduct, since both the carbonyl and cyano groups may be expected to exert magnetic anisotropy effects on the ethylidene moiety.[14] However, it may be suggested that the major **3** has an exo configuration on the basis of the estimated dihedral angles (θ) of the H-C-C-CN (134°) and H-C-C-CO (19°) fragments.[15] In fact, the fairly high isomer ratio appears to reflect the steric repulsion between the methyl group and the bulky quinone moiety.

A bicyclic dione **3** may be given by the dipolar addition of **1** to the cyano-substituted C=C bond and the subsequent release of nitrogen. Compound **4** is a usual product of the reaction of **1** and 2,3-dichloro-5,6-dicyanohydroquinone (DDQH$_2$), which indicates the reduction of DDQ during the reaction. Such a hydroquinone diether as **4** has already been obtained in a high yield by Eistert et al. in the reaction of **1** with chloranil.[16]

Unlike chloranil,[16] DDQ was found to react with **1** at the cyano-substituted C=C bond because of the reduced steric hindrance as well as the favorable LUMO energy for the dipolar addition.[17]

Reaction with Phenyldiazomethane. The reaction of DDQ with 1.6 equiv of phenyldiazomethane (**6**) mainly produced bicyclic diones (**7**, isomer ratio=5 : 1), together with stilbenes (**8**, cis/trans=0.8) (Scheme 3).

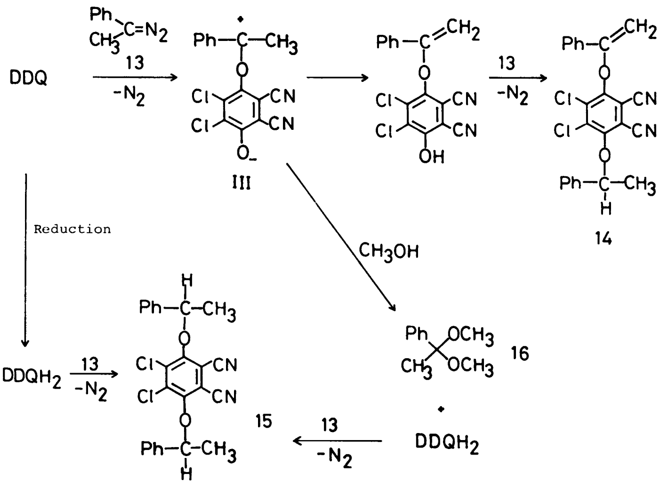


Scheme 3.

The structure of **7** was also established by the chemical conversion into the substituted cycloheptatriene (**9b**) (Scheme 2). The stereochemistry of **7** is unknown, but it is also likely that the major isomer is an exo adduct and that the much higher isomer ratio (=5) than in **3** is to be ascribed to the more enhanced steric repulsion between the phenyl group and the quinone moiety, by analogy with the case of **3**.

The formation of **8** can be explained by considering the participation of a 1 : 1 betaine intermediate, by analogy with our preceding reaction of **6** with chloranil.[8] According to the previous mechanism, the betaine I leads to the diazonium betaine(II) by the attack of another **6**, and subsequent El- and E2-type elimination (Path A) can afford **8**. On the other hand, intramolecular cyclization (Path B) is expected to build up spirooxetane (**10**). However, the DDQ reaction is somewhat different from the chloranil one in that the former gave no spirooxetane and provided more trans isomer for **8**, while the latter provided more *cis*-**8**. These phenomena may be ascribed mainly to the electronic effects of these two quinones.[18] The more electronegative DDQ moiety tends to destabilize II, thereby increasing the proportion of El elimination, mostly leading to *trans*-**8**. On the other hand, the predominant occurrence of E2-type elimination would result in the high cis to trans ratio of **8**, this is because of the steric reason mentioned previously for the chloranil reaction.[8] Moreover, the lack of spirooxetane in the present reaction must be due to its own instability, affected by the electronic factor, in the light of the relative bulkiness of these two quinones; the CN substituent of DDQ exerts less steric hindrance than the Cl substituent of chloranil.[19] Indeed, the spirooxetane of DDQ could not be obtained by the 3-h irradiation of a benzene solution (50 ml) of an equiv amount of DDQ (0.63 g, 2.8 mmol) and *trans*-**8** (0.50 g, 2.8 mmol) by using a high-pressure mercury lamp at 0 °C, though this photochemical method succeeded in providing a good yield of the *trans*-spirooxetane of chloranil.[8] Supporting the mechanistic explanation presented above, I reacted with added methanol to yield benzaldehyde dimethyl acetal (**11**) and DDQH$_2$. However, the dipolar addition to the C=C bond was not essentially affected, as is indicated by the 65% yield of **7**.

Reaction with 1-Phenyldiazoethane. The reaction of DDQ with 1-phenyldiazoethane (**13**) gave the (ethenyloxy)ethoxybenzene derivative (**14**, 92%) by a reaction sequence involving 1 : 1 betaine(III) formation, proton migration, and etherification with excess diazoalkane (Scheme 4). This reaction was accompanied by a small amount of a product from **13** and DDQH$_2$, 2,3-dichloro-5,6-dicyanohydroquinone bis(α-methylbenzyl) ether (**15**), as in the case of diazoethane.



Scheme 4.

In contrast to phenyldiazomethane, neither bicyclic diones nor dimeric olefins were yielded in this case. The marked change in the reaction fashion must be caused by the additional methyl substituent on the diazo-carbon, which will serve to increase the steric repulsion both on the dipolar addition to the C=C bond and on the nucleophilic attack upon the cation center of III responsible for the formation of the bicyclic dione and dimeric olefin respectively. These situations resulted in the exclusive addition to the C=O bond and the following proton migration, just as in the chloranil reaction.[10] Expectedly, added methanol

Table 1. Reactivities of Diazoalkanes in the Reactions with DDQ and Chloranil[a)]

	CH_2N_2	CH_3CHN_2	$PhCHN_2$	$PhC(CH_3)N_2$	Ph_2CN_2
DDQ	C[b)]	C>R	C>O	O>R	O[c)]
Chloranil	O[d)]	R[e)]	O[f)]	O[g)]	O[h)]

a) C: C=C addition; O: C=O addition; R: Reduction. b) Ref. 11. c) Ref. 12. d) Ref. 7. e) Ref. 16. f) Ref. 8. g) Ref. 10. h) Ref. 9.

completely inhibited the proton migration and produced acetophenone dimethyl acetal (**16**) and DDQH$_2$.

In order to demonstrate that the reactions of diazoalkanes with DDQ are substantially controlled by the structural natures, we present again in the table the representative reaction features for a series of diazoalkanes in comparison with those of the comparable chloranil reactions.

Experimental

All the melting points were taken with a Laboratoty Devices Mel-Temp instrument and are uncorrected. The infrared spectra were recorded on a Hitachi 260-10 apparatus and on a Perkin Elmer 983 G spectrometer. The ^{1}H and ^{13}C NMR spectra were taken on a Varian EM 390 spectrometer and on a JEOL FX 90-Q spectrometer respectively. The mass spectral data were obtained with a Hitachi RMU 6E mass spectrometer.

Materials. The 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was of commercial origin and was recrystallized from dichloromethane or chloroform. The diazoethane (**1**),[20)] phenyldiazomethane (**6**),[21)] and 1-phenyldiazoethane (**13**),[22)] were prepared according to the procedure described in the literature. The oily **6** and **13** contained the corresponding azines formed by the spontaneous thermal decomposition in ca. 10 and 30% respectively, as detected in the ^{1}H NMR spectra. However, these azines remained unchanged when allowed to stand for 1 h with DDQ in benzene-d_6, as was confirmed by the NMR measurements. The benzene was refluxed over lithium aluminum hydride and was fractionated.

3,4-Dichloro-2,5-dioxo-7-methylbicyclo[4.1.0]hept-3-ene-1,6-dicarbonitrile (3) and 2,3-Dichloro-5,6-dicyanohydroquinone diethyl Ether (4). An ether solution of diazoethane was added, drop by drop, to a stirred solution of DDQ (800 mg, 3.52 mmol) in benzene (20 ml) at 25 °C until the deep orange-red color due to the CT band of DDQ and benzene disappeared. At that point, a crystalline precipitate was formed. After a further 1 h stirring, the precipitate was filtered off and washed with benzene (10 ml×3) to leave the major isomer **3** (403 mg, 45%): Mp 245—246 °C (from acetone); IR (KBr) 2269 (C≡N), 1702 (C=O), 1558 (C=C), 1260, 1178, 987, 792 cm^{-1}; ^{1}H NMR (acetone-d_6) δ=1.75 (d, J=6.2 Hz, 3H, CH$_3$), 3.77 (q, J=6.2 Hz, 1H, cyclopropyl H); ^{13}C NMR (acetone-d_6) δ=13.2 (CH$_3$), 39.3 ($\underline{C}$-CH$_3$), 40.1 ($\underline{C}$-CN), 111.8 (CN), 141.7 (C=C), 176.7 (C=O); MS, m/z 254 (M$^+$). Found: C, 47.22; H, 1.64; N, 10.94%. Calcd for $C_{10}H_4Cl_2N_2O_2$: C, 47.09; H, 1.58; N, 10.98%.

The filtrate and the washing were then combined and evaporated to dryness. The residue was column chromatographed on silica gel. Elution with petroleum ether-benzene (1 : 1) gave **4** (87 mg, 9%): Mp 101—102 °C (from petroleum ether); IR (KBr) 2237 (C≡N), 1431, 1383, 1357, 1022, 926 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.50 (t, J=7.0 Hz, 6H, 2×CH$_3$), 4.27 (q, J=7.0 Hz, 4H, 2×methylene); MS, m/z 284 (M$^+$). Found: C, 50.64; H, 3.57; N, 9.77%. Calcd for $C_{12}H_{10}Cl_2N_2O_2$: C, 50.55; H, 3.54; N, 9.83%.

Further elution with benzene subsequently yielded a second crop of the major isomer **3** (90 mg, 10%) and the minor **3** (142 mg, 16%): Mp 236—238 °C (from acetone); IR (KBr) 2260 (C≡N), 1688 (C=O), 1556 (C=C), 1253, 1168, 802 cm^{-1}; ^{1}H NMR (acetone-d_6) δ=1.63 (d, J=6.8 Hz, 3H, CH$_3$), 3.53 (q, J=6.8 Hz, cyclopropyl H); MS, m/z 254 (M$^+$). Found: C, 47.08; H, 1.63; N, 10.75%. Calcd for $C_{10}H_4Cl_2N_2O_2$: C, 47.09; H, 1.58; N, 10.98%. Finally, an unidentified black powder (110 mg, mp>300 °C, IR (KBr) 3440, 1625, 1524 cm^{-1}) was eluted, with benzene-acetone (1 : 1) as the eluent.

Hydrogenation of 3. 3,4-Dichloro-2,5-dimethoxy-7-methyl-1,3,5-cycloheptatriene-1,6-dicarbonitrile (5b). The major isomer **3** (150 mg, 0.59 mmol) was hydrogenated with palladium carbon (100 mg, ca. 10%) at 25 °C in 1,4-dioxane (10 ml) under a hydrogen atmosphere. After 6 h stirring, the filtration of the catalyst and the evaporation of the solvent in vacuo gave a colorless solid (140 mg) showing a strong OH band at 3220 cm^{-1}. The treatment of the crude product with excess ethereal diazomethane and the subsequent column chromatography on silica gel, with benzene-ether (10 : 1) as an eluent, provided **5b** (108 mg, 64%): Mp 136—137 °C (from petroleum ether-benzene); IR (KBr) 2220 (C≡N), 1593 (C=C), 1309, 1280, 1058, 782 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.56 (d, J=7.0 Hz, 3H, CH$_3$), 2.63 (q, J=7.0 Hz, 1H, methine), 3.93 (s, 6H, 2×OCH$_3$); MS, m/z 284 (M$^+$). Found: C, 50.51; H, 3.53; N, 9.74%. Calcd for $C_{12}H_{10}Cl_2N_2O_2$: C, 50.55; H, 3.54; N, 9.83%.

The same workup converted the minor isomer **3** (80 mg) into **5b** (53 mg, 59%).

3,4-Dichloro-2,5-dioxo-7-phenylbicyclo[4.1.0]hept-3-ene-1,6-dicarbonitrile (7) and Stilbene (8). To a stirred solution of DDQ (480 mg, 2.1 mmol) in benzene (10 ml), we added, drop by drop at 25 °C over a 10-min period, a solution of phenyldiazomethane (400 mg, 3.4 mmol) in benzene (5 ml). After 1 h stirring, the precipitate was filtered off and washed with benzene (10 ml×3) and ether (5 ml×2) to leave the major **7** (280 mg, 42%): Mp 215—216 °C (from methanol); IR (KBr) 2253 (C≡N), 1707 (C=O), 1559 (C=C), 1172, 834 cm^{-1}; ^{1}H NMR (acetone-d_6) δ=5.16 (s, 1H, cyclopropyl H), 7.1—7.6 (m, 5H, Ph); MS, m/z 316 (M$^+$). Found: C, 56.91; H, 1.97; N, 9.01%. Calcd for $C_{15}H_6Cl_2N_2O_2$: C, 56.81; H, 1.91; N, 8.83%.

The filtrate and the washing were then combined, and the solvent was evaporated. A slight amount of the residue was submitted to HPLC analysis in order to determine the cis to trans ratio of **8** according to the previous procedure.[23)] The rest of the residue was chromatographed on silica gel. Elution with petroleum ether-benzene (5 : 1) gave a mixture of *cis* and *trans*-**8** (78 mg, 25%, based on the **6** used). The increasing benzene content provided, successively, benzaldehyde azine, a second crop of the major isomer **7** (110 mg, 17%), and the minor isomer **7** (80 mg, 12%): Mp 208—209 °C (from methanol); IR (KBr) 2256 (C≡N), 1699 (C=O), 1548 (C=C), 1182, 836 cm^{-1}; ^{1}H NMR (acetone-d_6) δ=5.03 (s, 1H, cyclopropyl H), 7.4—7.7 (m, 5H, Ph); MS, *m*/*z* 316 (M$^+$). Found: C, 57.12; H, 1.91; N, 8.75%. Calcd for $C_{15}H_6Cl_2N_2O_2$: C, 56.81; H, 1.91; N, 8.83%.

Hydrogenation of 7. 3,4-Dichloro-2,5-dimethoxy-7-phenyl-1,3,5-cycloheptatriene-1,6-dicarbonitrile (9b). The major isomer **7** (230 mg, 0.73 mmol) was hydrogenated with palladium carbon (100 mg) at 25 °C in 1,4-dioxane (20 ml) under a hydrogen atmosphere. After 6 h stirring, the catalyst was filtered off and the solvent was evaporated. We were unsuccessful in our attempt to crystallize **9a**, so the hydrogenated product was methylated with diazomethane and column chromatographed on silica gel, with benzene-ether (10 : 1) as the eluent, to give **9b** (175 mg, 69%): Mp 158—160 °C (petroleum ether); IR (KBr) 2190 (C≡N), 1591 (C=C), 1291, 946 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.93 (s, 6H, $2\times OCH_3$), 4.40 (s, 1H, methine), 7.27 (s, 5H, Ph); MS, *m*/*z* 346 (M$^+$). Found: C, 58.76; H, 3.47; N, 8.03%. Calcd for $C_{17}H_{12}Cl_2N_2O_2$: C, 58.80; H, 3.48; N, 8.07%.

Benzaldehyde Dimethyl Acetal (11) and 2,3-Dichloro-5,6-dicyanohydroquinone Dibenzyl Ether (12). To a stirred solution of DDQ (480 mg, 2.1 mmol) in benzene (10 ml) containing methanol (0.50g, 16 mmol), we added, drop by drop at 25 °C over a 10-min period, a solution of phenyldiazomethane (**6**) (400 mg, 3.4 mmol) in benzene (5 ml). After 1 h stirring, a precipitate was filtered off and washed with benzene (10 ml×3) and ether (5 ml×2). The crystalline product was assigned to the major isomer **7** (280 mg, 42%) on the basis of the IR analysis. The evaporation of the combined filtrate and washing in vacuo gave an pasty residue, the ^{1}H NMR spectrum of which showed the presence of benzaldehyde dimethyl acetal (**11**) (10%, as determined by the integral ratios, with 1,1,1,2-tetrachloroethane as the internal standard). This acetal was easily degradated to benzaldehyde and methanol on 1 d standing in the NMR tube, as confirmed by the disappearance of the acetal signal: ($CDCl_3$) δ=3.30 (s, 6H, $2\times OCH_3$) and 5.37 (s, 1H, methine). The column chromatographic treatment of the residue, with petroleum ether-benzene (20 to 100%) as eluents, gave, successively, benzaldehyde (16 mg, 7%), benzaldehyde azine, **12** (110 mg, 13%), the second crop of the major isomer **7** (80 mg, 12%), and the minor isomer **7** (70 mg, 11%). Compound **12** had a mp of 192—194 °C (from benzene): IR (KBr) 2228 (C≡N), 1421, 1355, 993 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.28 (s, 4H, methylene), 7.2—7.6 (m, 10H, 2×Ph); MS, *m*/*z* 408 (M$^+$). Found: C, 64.51; H, 3.44; N, 7.09%. Calcd for $C_{22}H_{14}Cl_2N_2O_2$: C, 64.56; H, 3.45; N, 6.85%.

2,3-Dichloro-5,6-dicyano-1-(1-phenylethenyloxy)-4-(1-phenylethoxy)benzene (14) and 2,3-Dichloro-5,6-dicyanohydroquinone bis(α-methylbenzyl) Ether (15). To a stirred solution of DDQ (0.50 g, 2.2 mmol) in benzene (10 ml), we added, drop by drop at 25 °C and over a 10-min period, a solution of 1-phenyldiazoethane (0.80 g, 6.1 mmol) in benzene (10 ml). After 6 h stirring, the evaporation of the solvent gave a brown solid. The ^{1}H NMR spectrum of this residue showed the formation of **14** and **15** in yields of 92 and 4% respectively, as determined by using 1,1,1,2-tetrachloroethane as the internal standard. Column chromatography on silica gel gave, successively, **15** and **14** by using petroleum ether-benzene (1 : 2). Compound **14** had a mp of 126—127 °C (from petroleum ether-benzene); IR (KBr) 2238 (C≡N), 1637 (C=C), 1420, 1268, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.82 (d, *J*=6.3Hz, 3H, CH_3), 3.77 (d, *J*=4.3Hz, 1H, olefinic H), 4.90 (d, *J*=4.3Hz, 1H, olefinic H), 5.80 (q, *J*=6.3Hz, 1H, methine), 7.2—7.8 (m, 10H, 2×Ph); MS, *m*/*z* 434 (M$^+$). Found: C, 65.99; H, 3.91; N, 6.47%. Calcd for $C_{24}H_{16}Cl_2N_2O_2$: C, 66.22; H, 3.71; N, 6.44%.

Compound **15** was identified by a comparison of its IR spectrum with that of an authentic specimen prepared by the treatment of 1-phenyldiazoethane with $DDQH_2$, having a mp of 119—120 °C (from benzene); IR (KBr) 2236 (C≡N), 1420, 1242, 1057, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.73 (d, *J*=6.3 Hz, 6H, $2\times CH_3$), 5.65 (q, *J*=6.3 Hz, 2H, 2×methine), 7.37 (s, 10H, 2×Ph); MS, *m*/*z* 332 ($M^+-PhCH=CH_2$). Found: C, 65.95; H, 4.09; N, 6.37%. Calcd for $C_{24}H_{28}Cl_2N_2O_2$: C, 65.91; H, 4.15; N, 6.41%.

Acetophenone Dimethyl Acetal (16). To a stirred solution of DDQ (1.0 g, 4.4 mmol) in benzene (20 ml), we added, drop by drop, at 25 °C and over a 10-min period, a solution of 1-phenyldiazoethane (0.70 g, 5.3 mmol) and methanol (1.0 g, 31 mmol) in benzene (10 ml). After 1 h stirring, the solvent was evaporated to dryness and the yield of **16** (69%) was determined by the integration of the methoxyl signals at δ 3.13 by using 1,1,1,2-tetrachloroethane as a standard in the ^{1}H NMR spectrum. Though the signals assignable to **15** were also observed, the two characteristic olefinic doublets (δ=3.77 and 4.90) attributable to **14** were not found, which is consistent with the complete inhibition of the proton migration process (see Scheme 4). The crude reaction mixture was extracted with pentane (20 ml×3) and the combined pentane solution was washed with 5% aqueous sodium carbonate (5 ml×3) and with NaCl saturated water (5 ml×2), dried over sodium sulfate, and concentrated in vacuo to give a pale yellow oil. Column chromatography on alumina, using pentane-benzene (9 : 1) as the eluent, gave **16** (260 mg, 36%): colorless oil; IR (film) 1277, 1148, 1044, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50 (s, 3H, CH_3), 3.13 (s, 6H, $2\times OCH_3$), 7.2—7.6 (m, 5H, Ph). Found: C, 72.47; H, 8.57%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

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