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Steric Effects in Photoinduced Electron Transfer Reaction of Halogenated 1,4-Benzoquinones with Donor Olefins

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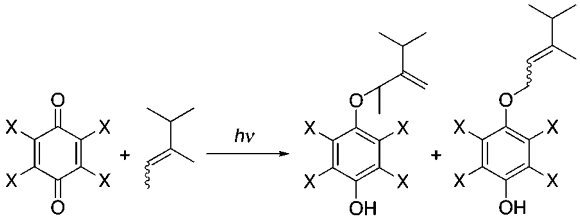
ABSTRACT



The photoinduced electron transfer reaction of halogenated 1,4-benzoquinones with 2,3-dimethyl-2-butene or 3,4-dimethyl-2-pentene gave the primary, secondary, and tertiary monoallyl ethers of hydroquinones, with the product distributions highly dependent on the steric nature of quinones and olefins.

The photoinduced electron transfer (PET) reaction has attracted much attention from a synthetic and theoretical viewpoint.[1] Irradiation of quinones with olefins is commonly utilized for the synthesis of [2 + 2] adducts, cyclobutanes and oxetanes.[2] Such a reaction of halogenated quinones with electron-rich olefins is expected to proceed through a PET reaction in view of the redox potentials of these components. Recently, Kochi et al. proposed[3] that the photoreaction of chloranil with stilbene in benzene proceeds via an electron-transfer mechanism to give the corresponding oxetanes. However, Xu et al. reported that the irradiation of chloranil with cyclohexene affords a hydroquinone monoallyl ether instead of oxetane.[4] Another aliphatic donor olefin, i.e., 2,3-dimethyl-2-butene, is also known to undergo PET with various acceptors, such as dicyanobenzene,[5] benzoyl cyanide,[6] 1,2-diketone,[7] and ketoester,[8] to give the corresponding mixture of primary (1°) and tertiary (3°) radical coupling products with acceptors in each case. In the present study, we found that photoreaction of unsubstituted **1a** and halogenated 1,4-benzoquinones **1b**−**d** with 2,3-dimethyl-2-butene **2a** or *cis*- and *trans*-3,4-dimethyl-2-pentene **2b** gave oxetane **5a** (only for **1a**), with the mixture of 1°, 2°, and 3° monoallyl ethers of hydroquinones markedly dependent on the steric nature of the quinones as well as the olefins.

The photoreaction of **1a**−**d** (100 mM for **1a** and **1b**, 50 mM for **1c** and **1d**) with a 5 equiv excess of **2a** was carried

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[1] (a) Kavarnos, G. J., Ed. *Fundamentals of Photoinduced Electron Transfer*; Wiley: New York, 1993. (b) Fox, M. A.; Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988.

[2] Maruyama, K.; Osuka, A. In *The chemistry of the quinonoid compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Volume 2, Chapter 13, p 759.

[3] (a) Sun, D.; Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **1999**, *64*, 2250. (b) Hubig, S. M.; Sun, D.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1999**, 781.

[4] Xu, J.-H.; Song, Y.-L.; Zhang, Z.-G.; Wang, L.-C.; Xu, J.-W. *Tetrahedron* **1994**, *50*, 1199.

[5] Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785.

[6] Cantrell, T. S. *J. Chem. Soc., Chem. Commun.* **1975**, 637.

[7] Turro, N. J.; Shima, K.; Chung, C.-J.; Tanielian, C.; Kanfer, S. *Tetrahedron Lett.* **1980**, *21*, 2775.

[8] Shima, K.; Sawada, T.; Yoshinaga, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 608.

[9] Filtration (>390 nm) causes the selective excitation of quinones and possible CT complexes with **2a**. For example, the mixture of **1c** (10 mM) and a 100 equiv excess of **2a** in acetonitrile showed a definite CT absorption at around $\lambda = 450$ nm by digital subtraction of **1c**.

[10] Gilbert et al. reported that a similar reaction gave only spiro-oxetane: Bryce-Smith, D.; Evans, E. H.; Gilbert, A.; McNeill, H. S. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1587.

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out at 20 °C under an argon atmosphere in benzene-d_6 by irradiation with a high-pressure mercury lamp through a >390 nm filter[9] (Scheme 1). Unsubstituted **1a** provided the 3° adduct, hydroquinone monoallyl ether **3a** (53% by NMR), along with spirooxetane **5a** (30%) upon 1 h irradiation (Table 1, entry 1).[10] However, the reaction of chloranil **1c** did not afford the corresponding oxetane but a mixture of 3° and 1° monoallyl ethers **3c** and **4c** in a ratio of 3:1 (entry 3). Compounds **3** and **4** were isolated by using HPLC, and the structures were determined by ^{1}H and ^{13}C NMR.[11] Since compound **3c** gradually decomposed, the structure was also confirmed as the O-methylated derivative **3c′** with diazomethane.[12] It is also noted that the reaction of fluoranil **1b** exclusively gave the 3° adduct **3b** (entry 2), while the reaction of bromanil **1d** gave a mixture of **3d** and **4d**, increasing the **4**/**3** ratio compared to that with **1c** (entry 4). Thus, the product distributions were very dependent on the identity of 1,4-benzoquinones. The reaction of **1a** with **2a** was also examined in acetonitrile to give a comparable amount of **5a** (24%) and **3a** (54%) for a 1 h reaction.[13]

Scheme 1

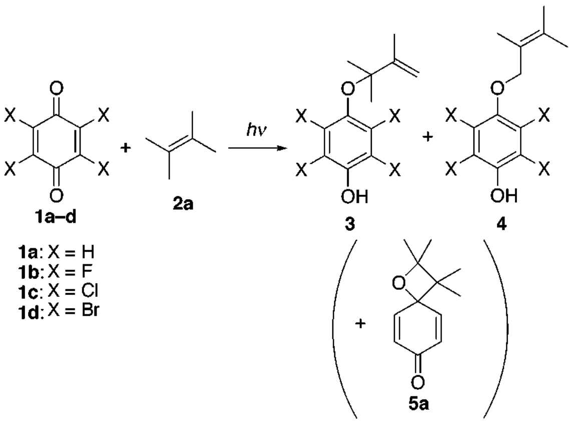


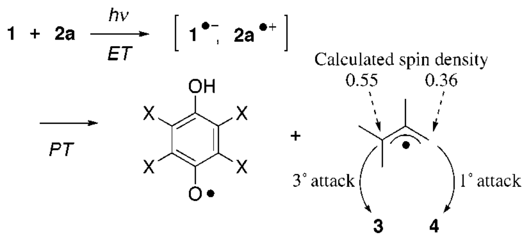
Table 1. Photoreaction of **1** with **2a** in Benzene-d_6

entry	1	time/h	yield/%[a] 3	4	5
1	**1a**	1	53 (54)[b]		30 (24)[b]
2	**1b**	2	89		
3	**1c**	1	71	24	
4	**1d**	1	54	40	

[a] Determined by ^{1}H NMR. [b] Values in parentheses are obtained in acetonitrile-d_3.

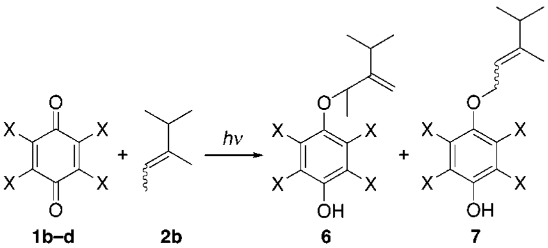
Mechanistically, the present photoreaction of **1** can be envisaged to proceed via PET because a free energy change of an electron transfer ΔG_{ET} deduced from the Rehm−Weller equation[14] is very negative for **1c** (−18.7 kcal) with **2a**, although the relevant value for **1a** is slightly positive (+2.5 kcal).[15] The radical ion pairs thus generated by the PET would lead to the phenoxy and allyl radical with (1°, 3°) termini via a proton transfer (PT)and finally collapse to the hydroquinone monoallyl ethers **3** and **4** by way of 3° and 1° attack, respectively (Scheme 2).

Scheme 2



Considering the increasing atomic radii of the quinone substituent, H (0.3 Å) < F (0.6) < Cl (0.99) < Br (1.14), as well as the calculated spin density of the allyl radical,[16] the smaller H or F substituted phenoxy radical would tend to exclusively attack the 3° carbon atom of high spin density and provide the corresponding monoallyl ether **3**. However, the larger Cl or Br substituted radical would exhibit the duality in radical attack associated with a critical balance of the steric repulsion and the spin density. Therefore, the bulkiest compound, **1d**, provided a significant amount of **4** due to the enhanced competitive attack on the less hindered 1° carbon atom possessing a low spin density. In regard to the formation of oxetane **5a**, it is not clear whether the PET mechanism[3] can explain the [2+ 2] addition or not because of the subtle value of ΔG_{ET}.

Scheme 3



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(11) **3c:** oil; ^{1}H NMR (C_6D_6) δ 1.27 (s, 6H), 2.02 (s, 3H), 4.72 (s, 1H), 4.78 (s, 1H). **4c:** colorless needles; mp 153.5−154.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3H), 1.87 (s, 3H), 1.97 (s, 3H), 4.47 (s, 2H), 6.03 (s, -OH); ^{13}C NMR δ 17.3, 20.7, 21.9, 74.6, 118.8, 123.4, 127.7, 133.1, 145.2, 146.0; MS (EI) *m/z* 328 (M^+, Cl = 35). Anal. Calcd for $C_{12}H_{12}O_2Cl_4$: C, 43.67; H, 3.66. Found: C, 43.44; H, 3.65.

(12) **3c′:** oil; ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 6H), 2.05 (s, 3H), 3.89 (s, 3H), 4.82 (s, 1H), 4.90 (s, 1H); ^{13}C NMR δ 19.2, 26.8, 60.8, 88.3, 109.2, 127.1, 129.6, 148.2, 149.6, 150.0; HRMS (CI) *m/z* ($(M+H)^+$) calcd for $C_{13}H_{15}O_2Cl_4$ 344.9797, found 344.9794.

(13) However, similar reaction of **1c** and **1d** failed because of the very poor solubility in acetonitrile.

(14) See the calculation for ΔG_{ET} for benzene solution: Xue, J.; Xu, J.-W.; Yang, L.; Xu, J.-H. *J. Org. Chem.* **2000**, *65*, 30.

(15) E^{red} of **1a** (−0.50 V vs SCE) **1c** (0.02) and E^{ox} of **2a** (1.53) were obtained from ref 1b. $E_{00}{}^{\mathrm{T}}$ of **1a** and **1c** are 2.3 and 2.7 eV, respectively.

(16) Calculations using the PM3 method were performed with the MOPAC program using CS MOPAC Pro software (ver 4.0).

To assess this mechanism and the resulting steric effects, we employed *cis*- or *trans*-3,4-dimethyl-2-pentene **2b** in place of **2a** in a photoreaction similar to that of **1b**−**d** (Scheme 3). This olefin is interesting in that the possible abstraction of three different protons, H_a, H_b, and H_c, of $[\mathbf{2b}]^{\bullet+}$ would give rise to the corresponding three radicals, **A**, **B**, and **C**, respectively (Scheme 4). When **1b** was irradiated with *trans*-**2b**, the corresponding 2° adduct **6b** was formed in low yield (19%) (Table 2, entry 5). Formation of 1° adduct **7** could not be observed in an elaborate NMR analysis. However, tetrafluoro-1,4-hydroquinone was also obtained in a yield of 33%.[17] However, the bulky **1c** and **1d** yielded the 1° adducts **7c** and **7d** (both 45%) along with a small amount of **6c** (12%) and **6d** (8%), respectively (entries 6 and 7). In these reactions, however, a careful NMR analysis showed no indication of formation of intermingled adduct from the most stable (2°, 3°) radical, **C**. Incidentally, it was also found that the stereochemistry of **7** was retained at ≥96% for the reaction with *trans*-**2b** (entries 6 and 7), while considerable stereoisomerization was observed in the reaction with *cis*-**2b** (entry 8). Such stereorandomization can be accounted for by the geometrical isomerization of intermediacy $[\mathbf{2b}]^{\bullet+}$. These results indicate that the reaction of smaller **1b** causes H_a abstraction followed by radical coupling at the 2° center of **A** to produce **6**. On the other hand, bulky **1c** and **1d** prefer H_b abstraction (for **B**) to H_a abstraction (for **A**). The subsequent radical coupling is performed in such a way that the resulting **A** undergoes 2° attack and **B** 1° attack to afford **6** and **7**, respectively.

Scheme 4

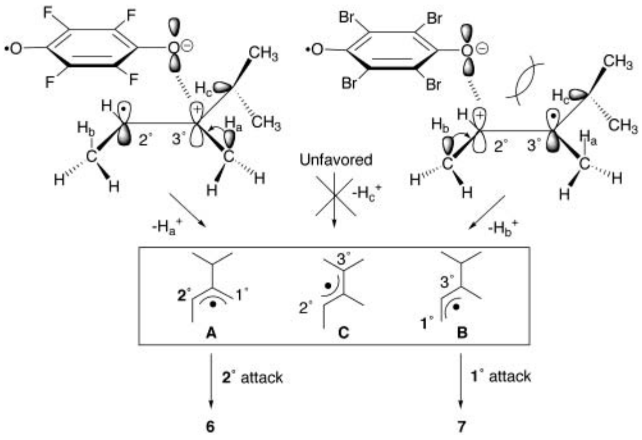

Table 2. Photoreaction of **1** with **2b** in Benzene-d_6

entry	**1**	**2b**	time/h	yield/%[a] **6**	**7**
5	**1b**	*trans*	5	19	
6	**1c**	*trans*	1	12	45 (96:4)[b]
7	**1d**	*trans*	1	8	45 (>99:1)[b]
8	**1c**	*cis*	1	10	40 (78:22)[b]

[a] Determined by ^{1}H NMR. [b] Ratio of *trans:cis*.

Why is the generation of **A** and **B** radicals dependent on the quinone substituent and why is the most stable allyl radical, **C**, not formed? This problem can be resolved by considering the geometrical structure at the stage of proton transfer from $[\mathbf{2b}]^{\bullet+}$ to the counter semiquinone radical. As depicted in Scheme 4, the calculated structure of $[\mathbf{2b}]^{\bullet+}$ has the highest spin density (0.40) on the 2° carbon atom and the relatively larger positive charge (+0.1) on the 3° carbon atom. The positive 3° carbon atom will be more stabilized by electrostatic interaction with the closely located less hindered semiquinone radical of **1b** (Scheme 4, left). This steric and electronic situation facilitates the adjacent H_a^+ abstraction to give radical **A**. In contrast to **1b**, on account of the severe steric repulsion with the isopropyl group of **2b**, the more separated bulky semiquinone radicals of **1c** and **1d** will induce the positive charge on the 2° carbon atom (Scheme 4, right) and preferentially bring about H_b^+ abstraction to yield radical **B**. Absence of the radical **C** product can be explained by stereoelectronic effects which inhibit the efficient $\sigma-\pi$ interaction between the C−H_c bond and the vacant p-orbital due to restricted orthogonal conformation.

In conclusion, the photoinduced electron-transfer reaction of halogenated 1,4-benzoquinones **1** with 2,3-dimethyl-2-butene **2a** or 3,4-dimethyl-2-pentene **2b** was markedly affected by the steric nature of the quinone substituents to provide the corresponding 1°, 2°, and 3° hydroquinone monoallyl ethers. The product distributions were rationalized in terms of steric effects on both H^+ abstraction from $[\mathbf{2b}]^{\bullet+}$ and recombination of generated allyl and phenoxy radicals as well as the spin density.

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[17] In ref 4, the corresponding hydroquinone was similarly formed in the photoreaction of **1c** with cyclohexene in 46% yield.