DIHYDROBENZOFURANS *VIA* DIENONE-PHENOL REARRANGEMENT OF SPIROOXETANES FROM PHOTOADDITION OF QUINONES WITH ELECTRON DONOR OLEFINS

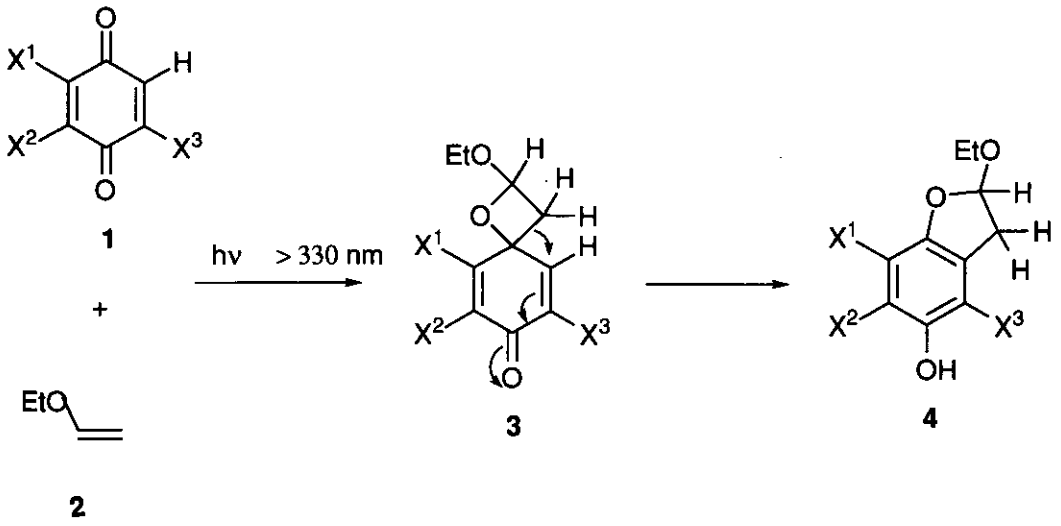
Takumi Oshima*, Yu-ichi Nakajima, and Toshikazu Nagai
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Toyonaka, Osaka 560, Japan

Abstract- Photoaddition of electron donor olefins such as vinyl ethers and stilbene to variously methyl- and halogeno-substituted 1,4-benzoquinones resulted in the formation of dihydrobenzofurans *via* a dienone-phenol rearrangement of the primary product spirooxetanes.

Photoinduced [2+2] cycloadditions of quinones to olefins are known to give spirooxetanes or cyclobutanes depending on the structure of the respective quinone and olefin.[1] The spirooxetane formation shows the potential of a synthetic application as the Paterno-Büchi reaction. Recently, Gilbert *et al.* have described the photoaddition of parent 1,4-benzoquinone to a wide variety of electron donor and electron acceptor olefins.[1f] They explored the features which direct and control the regiochemistry of addition of the olefin to the quinone on the basis of a mechanism involving an initial photoelectron transfer to the quinones.[1f, 2] Using tetrachloro-1,4-benzoquinone, Xu and his co-workers have also made a better understanding of the scope of the photoinduced oxetane formation with stilbene and elucidated the factors that influence the reaction outcome.[3] However, a research interest regarding the synthetic utilization of the strained oxetane-ring connected with the conjugated dienone framework is surprisingly limited.

In this paper, we report that the title oxetanes (**3**) from various 1,4-benzoquinones (**1**) with ethyl vinyl ether (**2**) provide dihydrobenzofurans (**4**) *via* a dienone phenol rearrangement[4] as seen in Scheme 1.

Irradiation was carried out on quinones (**1**, 1.0 mmol) and 5 equiv. excess of **2** in dry benzene solution (10 ml) placed in a Pyrex tube ($\lambda > 330$ nm) under nitrogen at ordinary temperature by using a 300 W high-pressure mercury arc. The quinones were completely consumed for 2 h irradiation (by hplc).

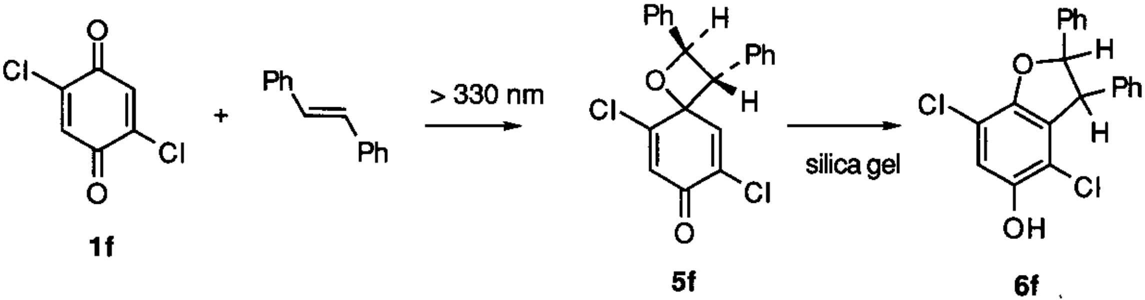


Scheme 1

The solvent and excess volatile **2** were evaporated in vacuo and the reaction mixtures were immediately submitted for ^{1}H nmr analysis. The signals assignable to the expected spirooxetanes (**3**) were not found, but dihydrobenzofurans (**4**) were detected. The results are shown in Table 1.

The structures of **4** were confirmed by ir, ^{1}H and ^{13}C nmr as well as elemental analysis. In particular, the ^{1}H nmr spectra revealed the abnormally low field methine quartet centered at δ 5.60-5.84 ppm, manifesting the presence of dioxamethylene linkage. Therefore, the regiochemistry of the primary spirooxetanes is opposite to that predicted from the relative stability of the two possible pre-oxetane 1,4-diradicals as in the usual photoaddition of vinyl ether to ketones.[5] The origin of such regioselective addition is explained by a polar exciplex resulting from an initial electron transfer to the quinone.[1f, g, 3] All quinones did not react with ethyl vinyl ether in the dark, and remained intact even on irradiation with acceptor olefin acrylonitrile.

When the donor olefin was replaced by trans-stilbene, we succeeded in isolating spirooxetane (**5f**) with 2,5-dichloro-*p*-benzoquinone (**1f**).[6] The oxetane (**5f**) did not spontaneously decompose to the corresponding furan probably because of steric hindrance due to the phenyl substituent, but easily underwent the rearrangement to afford almost quantitative furan (**6f**) on silica gel column chromatography (Scheme 2).



Scheme 2

As to the formation of dihydrobenzofurans from spirooxetanes of quinones, only a little is known. Wilson *et al.* have reported that upon irradiation with an argon laser source (in visible region) under one atmosphere oxygen in carbon tetrachloride, 1,4-benzoquinone with styrene provides 3-phenyldihydrobenzofuran (5%), along with 4'-phenyl substituted spirooxetane (9%) and trioxane product (56%).[1b] This furan is said to arise from the regioisomeric 3'-phenylspirooxetane. In contrast, it has been argued[1f] that with conventional light source (λ > 300 nm) in benzene under atmosphere of oxygen, this donor-acceptor system fails in yielding the reported furan, although this reaction gives the trioxane and 4'-phenylspirooxetane in a ratio closely similar to that earlier reported.[1b]

Table 1. Dihydrobenzofurans(**4**) *via* dienone-phenol rearrangement of spirooxetanes(**3**) from photocycloaddition of quinones(**1**) with ethyl vinyl ether (**2**)[a]

entry		Quinone(**1**) X^1	X^2	X^3	X^4	Yield(%)[b] **4**
1	**a**	H	H	Me	H	52 (21)[c]
2	**b**	Me	H	Me	H	46 (37)
3	**c**	H	Me	Me	H	45 (25)
4	**d**	H	H	Cl	H	35 (14)[c]
5	**e**	Cl	Cl	H	H	44 (25)
6	**f**	Cl	H	Cl	H	59 (32)
7	**g**	H	Cl	Cl	H	65 (37)
8	**h**	Cl	Cl	Cl	H	59 (26)
9	**i**	H	Br	Br	H	37 (33)

[a] Reactions were carried out by employing 5 equiv. excess of **2** in benzene for 2 h under nitrogen atmosphere with filtered irradiation(> 330 nm). [b] Determined by ^{1}H nmr integral ratio of the dioxamethylene peak area of **4** with respect to the methylene peak area of α-bromo-*p*-xylene as an internal standard and the values in parenthesis are isolated yields by silica gel column chromatography. In some cases, low isolated yields are due to the difficulty in performing the clear-cut chromatographic separation. [c] A small amount of isomeric furan was detected in ^{1}H nmr measurement, but it could not be isolated in pure form.

Finally, we consider the possible formation of furan from the photo reaction of the parent 1,4-benzoquinone with ethyl vinyl ether. Gilbert *et al.* obtained 4'-ethoxyspirooxetane with filtered radiation (λ > 300 nm), albeit in low yield (4%).[1f] In an effort to get the furan under our photolytic conditions, the reaction mixtures were found to certainly contain a considerable amount of the spirooxetane reported by Gilbert,[1f] but neither the oxetane nor the aimed furan was obtained on usual chromatographic treatment which gave only intractable resinous products.

In summary, the new finding of this study is that the spirooxetanes from photo reaction of substituted 1,4-benzoquinones with vinyl ethers and stilbene undergo a dienone-phenol rearrangement to provide dihydrobenzofurans (with acidic assistance for stilbene).

EXPERIMENTAL

All mps were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer 983G spectrophotometer. ^{1}H- and ^{13}C-nmr spectra were obtained on a JEOL EX-270 MHz instrument. Mass spectra were taken on a JEOL JMS DX303 mass spectrometer.

The general procedure is represented for the reaction of **1a** (100 mg) and 5 equiv. excess of ethyl vinyl ether (300 mg) in benzene (10 ml). After 2 h's filtered irradiation (> 330 nm) under nitrogen atomosphere, the volatile materials were evaporated and the residue was submitted for ^{1}H nmr analysis to determine the yield of dihydrofuran (**4a**) by using an internal standard, α-bromo-*p*-xylene. The reaction mixture was chromatographed to give the furan (**4a**) with a mixture of hexane-benzene(3:7 by volume) as an eluent. The reaction of 2,5-dichloro-*p*-benzoquinone (**1f**) with trans-stilbene were similarly carried out by irradiation of a solution of **1f** (300 mg) and 1.2 equiv. of stilbene (360 mg) in benzene (10 ml) for 30 h. After evaporation of the solvent, pure trans-spirooxetane (**5f**, 150 mg, 25%) was obtained by washing the residues with pentane and then by recrystallization from benzene. The stereochemistry of **5f** was confirmed by the thermal [2+2] cycloreversion to trans-stilbene and quinones **1f**.[7] However, column chromatographic treatment of the reaction residues on silica gel gave no **5f** but the rearranged diphenylbenzofuran (**6f**, 180 mg, 30%).

2-Ethoxy-2,3-dihydro-5-hydroxy-4-methylbenzofuran (4a): mp 97-98℃, colorless prisms (from benzene); ir(KBr) 3393, 2981, 1460, 1378, 1355, 1267, 1192, 1113, 1072, 946, 717 cm^{-1}; ^{1}H-nmr δ 6.56(d, J=8.6 Hz, 1H), 6.52(d, J=8.6 Hz, 1H), 5.72(dd, J_1=6.6, J_2=2.0 Hz, 1H), 4.53(s, 1H, OH), 3.93(dq, J_1=14.2, J_2=6.9 Hz, 1H), 3.63(dq, J_1=14.2, J_2=6.9 Hz, 1H), 3.24(dd, J_1=16.5, J_2=6.6 Hz, 1H), 2.95(dd, J_1=16.5, J_2=2.0 Hz, 1H), 2.12(s, 3H), 1.24(t, J=6.9 Hz, 3H); ^{13}C-nmr δ 151.5, 148.0, 125.7, 121.2, 113.9, 106.7, 106.1, 64.0, 36.4, 15.1, 12.7; mass m/z 194 (M^+). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.06; H, 7.00. Found: C, 68.02; H, 7.26.

2-Ethoxy-2,3-dihydro-5-hydroxy-4,7-dimethylbenzofuran (4b): mp 112-112.5 ℃ , colorless prisms (from benzene); ir(KBr) 3444, 2971, 1493, 1443, 1361, 1180, 1110, 1067, 932, 782, 693 cm^{-1}; ^{1}H nmr δ 6.41(s, 1H), 5.71(dd, J_1=6.6, J_2=2.0 Hz, 1H), 4.28(s, 1H, OH), 3.93(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.63(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.23(dd, J_1=16.5, J_2=6.6 Hz, 1H), 2.94(dd, J_1=16.5, J_2=2.0 Hz, 1H), 2.15(s, 3H), 2.09(s, 3H), 1.24(t, J=7.3 Hz, 3H); ^{13}C nmr δ 150.0, 147.8, 124.9, 117.9, 117.0, 115.4, 105.7, 63.8, 36.6, 15.1, 14.9, 12.4; mass m/z 208 (M^+). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 69.03; H, 7.70.

2-Ethoxy-2,3-dihydro-5-hydroxy-4,6-dimethylbenzofuran (4c): 112-112.5℃, colorless prisms (from benzene); ir(KBr) 3429, 2930, 1461, 1365, 1342, 1259, 1176, 1112, 1083, 938, 784 cm^{-1}; ^{1}H nmr δ

6.41(s, 1H), 5.62(dd, J_1=6.6, J_2=2.0 Hz, 1H), 4.17(s, 1H, OH), 3.82(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.55(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.15(dd, J_1=16.5, J_2=6.6 Hz, 1H), 2.88(dd, J_1=14.2, J_2=7.3 Hz, 1H), 2.13(s, 3H), 2.06(s, 3H), 1.16(t, J=7.3 Hz, 3H); ^{13}C nmr δ 151.2, 146.2, 122.9, 122.3, 120.5, 108.5, 105.9, 63.8, 36.4, 16.4, 15.1, 12.9; mass m/z 208(M^+). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 69.42; H, 7.96.

4-Chloro-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4d): Colorless oil; ir(KBr) 3434, 2974, 1465, 1372, 1349, 1275, 1189, 1114, 1085, 940, 704 cm^{-1}; ^{1}H-nmr δ 6.80(d, J=8.6 Hz, 1H), 6.65(d, J=8.6 Hz, 1H), 5.74(dd, J_1=6.6, J_2=2.3 Hz, 1H), 5.07(s, 1H, OH), 3.91(dq, J_1=14.2, J_2=6.9 Hz, 1H), 3.63(dq, J_1=14.2, J_2=6.9 Hz, 1H), 3.34(dd, J_1=17.2, J_2=6.6 Hz, 1H), 3.07(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.24(t, J=6.9 Hz, 3H); ^{13}C-nmr δ 152.0, 145.7, 124.5, 116.6, 114.8, 108.6, 106.2, 64.2, 37.0, 15.0; mass m/z 214 (M^+, Cl=35). Anal. Calcd for $C_{10}H_{11}O_3Cl$: C, 55.96; H, 5.17. Found: C, 56.18; H, 5.03.

6,7-Dichloro-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4e): mp 109-110℃, colorless prisms (from benzene); ir(KBr) 3357, 2975, 1452, 1376, 1352, 1263, 1188, 1113, 1078, 940, 704 cm^{-1}; ^{1}H-nmr δ 6.76(s, 1H), 5.75(dd, J_1=6.6, J_2=2.3 Hz, 1H), 5.41(s, 1H, OH), 3.90(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.63(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.33(dd, J_1=17.2, J_2=6.3 Hz, 1H), 3.06(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.23(t, J=7.3 Hz, 3H); ^{13}C-nmr δ 151.3, 142.2, 119.2, 117.7, 117.6, 109.0, 107.0, 64.4, 36.9, 15.0; mass m/z 248 (M^+, Cl=35). Anal. Calcd for $C_{10}H_{10}O_3Cl_2$: C, 48.22; H, 4.05. Found: C, 48.18; H, 4.07.

4,7-Dichloro-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4f): mp 105-106℃, colorless prisms, (from benzene); ir(KBr) 3354, 2977, 1452, 1376, 1351, 1188, 1113, 1078, 940, 796, 704 cm^{-1}; ^{1}H-nmr δ 6.76(s, 1H), 5.75(dd, J_1=6.6, J_2=2.3 Hz, 1H), 5.38(s, 1H, OH), 3.90(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.63(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.32(dd, J_1=17.2, J_2=6.6 Hz, 1H), 3.06(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.23(t, J=7.3 Hz, 3H); ^{13}C-nmr δ 151.4, 142.2, 124.6, 119.3, 117.7, 109.0, 106.5, 64.4, 36.9, 15.0; mass m/z 248 (M^+, Cl=35). Anal. Calcd for $C_{10}H_{10}O_3Cl_2$: C, 48.22; H, 4.05. Found: C, 47.98; H, 3.97.

4,6-Dichloro-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4g): mp 110.5-111℃, colorless prisms (from benzene); ir(KBr) 3406, 2945, 1469, 1440, 1355, 1185, 1135, 1086, 1013, 960, 698 cm^{-1}; ^{1}H-nmr δ 6.76(s, 1H), 5.75(dd, J_1=6.3, J_2=2.3 Hz, 1H), 5.42(s, 1H, OH), 3.90(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.63(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.32(dd, J_1=17.2, J_2=6.3 Hz, 1H), 3.06(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.23(t, J=7.3 Hz, 3H): ^{13}C-nmr δ 151.3, 142.2, 124.6, 119.3, 117.7, 108.9, 106.5, 64.4, 36.9, 15.0; mass m/z 248 (M^+, Cl=35). Anal. Calcd for $C_{10}H_{10}O_3Cl_2$: C, 48.22; H, 4.05. Found: C, 48.15; H, 4.08.

4,6,7-Trichloro-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4h): mp 136-137 ℃, colorless prisms (from benzene); ir(KBr) 3388, 2961, 1461, 1376, 1347, 1259, 1186, 1080, 1037, 931, 704 cm^{-1}; ^{1}H-nmr δ 5.84(dd, J_1=6.6, J_2=2.3 Hz, 1H), 5.51(s, 1H, OH), 3.98(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.68(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.41(dd, J_1=17.2, J_2=6.6 Hz, 1H), 3.15(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.25(t, J=7.3 Hz, 3H); ^{13}C-nmr δ 148.6, 143.2, 124.5, 118.5, 117.7, 115.9, 106.7, 64.9, 37.7, 15.0; mass m/z 282 (M^+). Anal. Calcd for $C_{10}H_9O_3Cl_3$: C, 42.36; H, 3.20. Found: C, 42.52; H, 3.24.

4,6-Dibromo-2-ethoxy-2,3-dihydro-5-hydroxybenzofuran (4i): mp 100-101℃, colorless prisms (from benzene); ir(KBr) 3446, 2935, 1460, 1415, 1347, 1188, 1171, 1091, 1014, 938, 697 cm^{-1}; ^{1}H-nmr δ 6.93(s, 1H), 5.74(dd, J_1=6.6, J_2=2.3 Hz, 1H), 5.46(s, 1H, OH), 3.90(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.63(dq, J_1=14.2, J_2=7.3 Hz, 1H), 3.28(dd, J_1=17.2, J_2=6.6 Hz, 1H), 3.00(dd, J_1=17.2, J_2=2.3 Hz, 1H), 1.23(t, J=7.3 Hz, 3H); ^{13}C-nmr δ 151.6, 143.7, 127.8, 122.2, 106.9, 106.6, 106.2, 64.4, 38.8, 15.0; mass m/z 336 (M^+, Br=79). Anal. Calcd for $C_{10}H_{10}O_3Br_2$: C, 35.54; H, 2.98. Found: C, 35.65; H, 3.03.

2,5-Dichloro-trans-3',4'-diphenylspiro[2,5-cyclohexadiene-1,2'-oxetane]-4-one (5f): mp 114-115℃, colorless prisms (from hexane-benzene); ir(KBr) 1674, 1012, 987, 957, 750, 701 cm^{-1}; ^{1}H-nmr δ 7.10-7.69(m, 11H), 6.65(s, 1H), 6.30(d, J=9.0 Hz, 1H), 4.93(d,J=9.0 Hz, 1H); mass m/z 356(M^+); Anal. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 67.24; H, 3.95. Found: C,67.27; H,4.02.

4,7-Dichloro-2,3-dihydro-5-hydroxy-2,3-diphenylbenzofuran (6f): mp 98-99℃, colorless needles (from hexane-benzene); ir(KBr) 3419, 1458, 1189, 858, 699 cm^{-1}; ^{1}H-nmr δ 7.11-7.55 (m, 10H), 6.97(s, 1H), 5.67(d, J=6.0 Hz, 1H), 5.07(s, OH, 1H), 4.62(d, J=6.0 Hz, 1H); mass m/z 356(M^+). Anal. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 67.24; H, 3.95. Found: C, 67.23; H, 4.13.

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