Notes

Oxyfunctionalization of Biphenylene by Singlet Oxygen, Hydrogen Peroxide/Methyltrioxorhenium, and Dimethyldioxirane

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Introduction

Cyclobutadiene (**1**), the smallest annulene, has continued to attract the interest of both experimental and theoretical chemists.[1] The cyclobutadiene unit may be stabilized by incorporating one or both of the double bonds into a benzene ring, as in benzocyclobutadiene (**2**)[2] and biphenylene (**3**),[3] the mono- and dibenzo derivatives of cyclobutadiene.
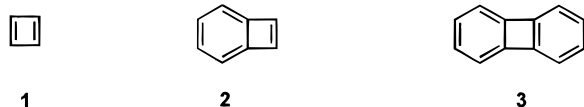
Both derivatives **2** and **3** have an overall 4n π-electron and might, therefore, be expected to show antiaromatic behavior. This holds for benzocyclobutadiene (**2**), which is observed only as a reactive intermediate. In contrast, biphenylene (**3**) is thermally stable and shows many of the properties associated with aromatic compounds. Thus, biphenylene (**3**) preferentially undergoes substitution rather than addition reactions, and it does not readily participate in Diels−Alder cycloadditions. It forms charge-transfer complexes with maleic anhydride and tetracyanoethylene; the latter does not give cycloadducts even on heating.[2b,4] However, **3** reacts with the more electron-deficient dienophile tetrachloro(fluoro)-benzyne but not with benzyne.[5]

While the endoperoxides of polycyclic aromatic compounds such as anthracenes and substituted naphtha-

Scheme 1
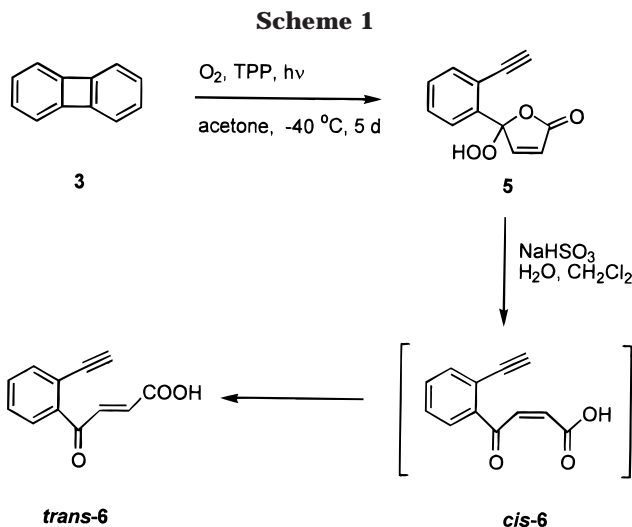
lenes are well-known, biphenylene endoperoxide **4**, formed by the [4 + 2]cycloaddition of singlet oxygen, has as yet not been reported. Biphenylene (**3**) is known to be inert to autoxidation but may be oxidized under forcing conditions to phthalic acid and to a number of unidentified products on treatment with osmium tetraoxide[6] or ozone.[7] Low yields of 2,3-biphenylenequinone (**12**) and several homolytic substitution products have been obtained by the reaction of **3** with either ceric ammonium nitrate,[8] lead tetraacetate,[9] or manganese(III) acetate.[10]

In this paper, we have examined the oxidation of biphenylene (**3**) by singlet oxygen, H_2O_2 activated with methyltrioxorhenium (MTO) as catalyst,[11] and dimethyldioxirane (DMD).[12] Our results show that unusual oxidation processes have been observed with these three oxidants.

Results and Discussion

Singlet Oxygen. Tetraphenylporphine-sensitized photooxygenation of arene **3** in acetone resulted in the hemiketal hydroperoxide **5** (Scheme 1). After chromatography on silica gel, **5** was isolated as the sole product in 56% yield. The structural assignment of the hydroperoxide **5** rests on its physical and chemical behavior.

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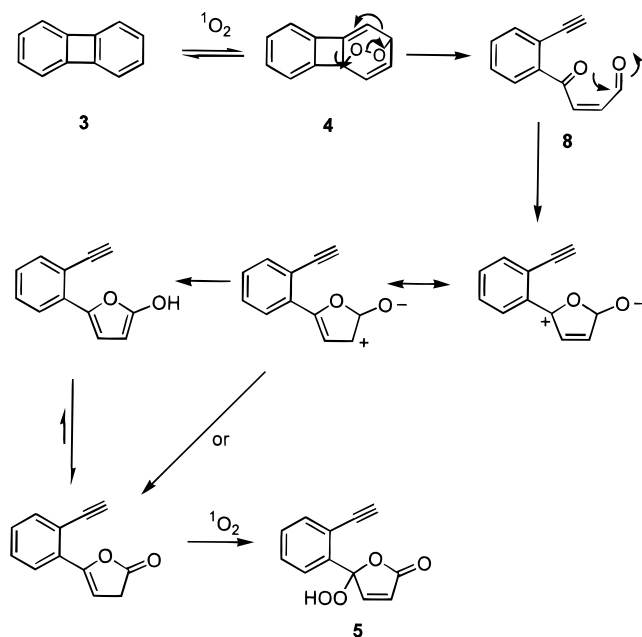
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Scheme 2

Scheme 3

Thus, the elemental analysis confirmed the molecular formula $C_{12}H_8O_4$,[13] while the lactone structure was established by its 250 MHz ^{1}H NMR, 63 MHz ^{13}C NMR, and IR spectra. The olefinic hydrogens display an AB-system at 8.12 and 6.37 ppm ($J = 5.6$ Hz) as required by the α,β-unsaturated carbonyl derivatives. Aromatic protons comprise a multiplet, and the singlet at 4.03 ppm belongs to the acetylenic proton with a large (252 Hz) J_{CH} coupling, as expected for acetylenic compounds. The hydroperoxide and lactone functional groups are indicated by the IR-spectral absorptions at 3276 and 1748 cm^{-1}. The ^{13}C NMR spectrum consisting of nine sp^2 carbon and two sp and one sp^3 carbon signals is in accord with the proposed structure.

To corroborate the structure chemically, hydroperoxide **5** was allowed to react with aqueous sodium bisulfite to afford the trans keto acid **6**. The olefinic protons display an AB system, and its large coupling constant ($J = 15.6$ Hz) clearly shows the trans configuration of the double bond in the cinnamic acid derivatives **6**. Furthermore, the ^{13}C NMR spectrum indicates the presence of two carbonyl groups (191.7 and 170.7 ppm), which again supports the assigned structure.

To elucidate the mechanistic details of this unusual process, the photooxygenation was conducted at −40 °C and monitored by ^{1}H NMR spectroscopy. The observed NMR data provide evidence for the bicyclic endoperoxide **4**, proposed to be formed in the initial step of this ^{1}O$_2$ reaction (Scheme 2). Thus, the observed AB system for the olefinic protons at 6.9−7.15 ppm (low-field part is further split by the bridgehead protons), the doublet at 6.6 ppm (other olefinic proton), and the triplet at 5.9 ppm (bridgehead proton) substantiate the structure of endoperoxide **4**.

As is evident, cycloaddition has taken place across the C-2/C-4a positions in biphenylene (**3**), which corroborates the theoretical product stabilities for the cycloaddition
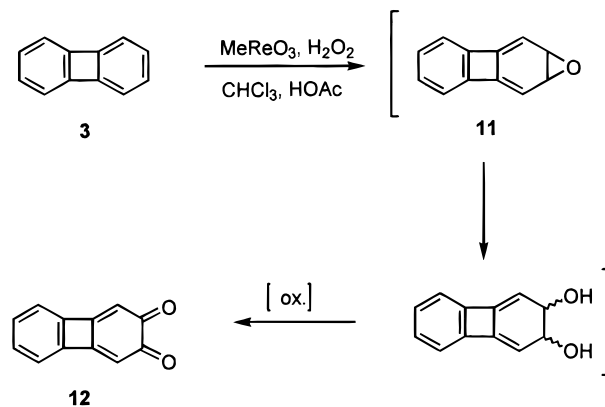
of maleic anhydride to biphenylene.[14] Furthermore, on warming to ca. 10 °C, the endoperoxide **4** underwent a retro-Diels−Alder reaction to give singlet oxygen and biphenylene. The ease of such molecular oxygen extrusion from polycyclic arenes depends on the nature of the aromatic system and on the type of substituents[15] and is favorable for the present.[16]

In competition with the retro-Diels−Alder reactions, endoperoxide **4** suffers electrocyclic fragmentation to the dicarbonyl product **8** (Scheme 2). The latter intermediate intramolecularly subsequently cyclizes to the corresponding furanol derivative **9**, which will be in equilibrium with its tautomeric 2(3H)-furanone **10**; additionally, **10** may be generated directly from **8** (Scheme 2). Ene reaction[17] of furanone **10** with singlet oxygen should finally lead to the observed hydroperoxide **5** as isolable product.

Hydrogen Peroxide/Methyltrioxorhenium (MTO). The oxidation of biphenylene (**3**) by hydrogen peroxide with a catalytic amount of methyltrioxorhenium (CH$_3$-ReO$_3$) in chloroform afforded the *o*-quinone **12** in 83% yield (20% conversion of **3**) at room temperature (Scheme 3). All observed spectral data were consistent with the reported ones.[8]

The formation of quinone **12** is rationalized in terms of the reaction path shown in Scheme 3. Epoxidation of the 2,3 bond in biphenylene leads first to the monoepoxide **11**;[18] the latter does not rearrange to the corresponding oxepin derivative due to its cyclobutadienic character.[19] Acid-catalyzed epoxide-ring opening, followed by oxidation of the diol with H$_2$O$_2$/MTO, presumably results finally in the *o*-quinone **12**.

Dimethyldioxirane (DMD). With dimethyldioxirane (DMD), a powerful oxidant under neutral conditions, after 1 day of oxidation, the biphenylene (**3**) was converted exclusively to the trisepoxide **13** to the extent of only 30%, as observed by ^{1}H NMR spectroscopy (Scheme 4). The ^{1}H NMR spectrum of the trisepoxide **13** displayed an AA′BB′ system, which was assigned to

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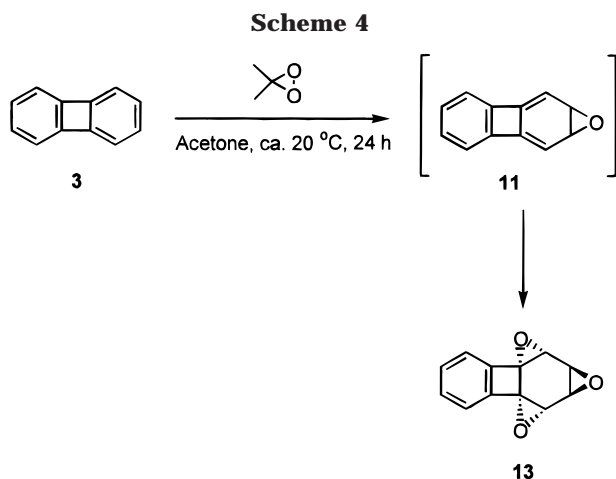(15) Balci, M. *Chem. Rev.* **1981**, *81*, 91−108.

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Scheme 4

3

11

13

the symmetrical benzo group. The epoxide protons appear as two separate singlets at 3.98 and 3.48 ppm, as expected for the trans configuration of the epoxide rings.[20]

These three oxidations show unequivocally that biphenylene (**3**) may be oxyfunctionalized under relatively mild conditions.

Experimental Section

Biphenylene was synthesized according to the literature.[21] Reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Acetone was stored over 4 Å molecular sieves before use. Melting points were taken on a Büchi apparatus. Solvents were concentrated at reduced pressure (ca. 20 °C, 20 Torr). Infrared spectra were obtained on KBr pellets by employing a Perkin-Elmer apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a 250 (63) MHz spectrometer. All column chromatography was performed on silica gel.

5-Hydroperoxy-5-(2-ethynylphenyl)furan-2-one (5). A sample of 1.0 g (6.57 mmol) of biphenylene and 50 mg of *meso*-tetraphenylporphine in 25 mL of acetone were photolyzed for 6 d at −40 °C with a 400 W sodium lamp while oxygen gas was bubbled through solution. After removal of the solvent, the mixture was chromatographed over silica gel (40 g) by elution with dichloromethane to afford 340 mg (2.23 mmol) of unreacted biphenylene and TPP. Further elution with ethyl ether gave 530 mg (2.45 mmol) of hydroperoxide **5** in 56% yield (relative to converted material, conversion. ca. 66%). Recrystallization from dichloromethane afforded a colorless solid, which exploded above 120 °C without melting: ^{1}H NMR (250 MHz, CD$_3$COCD$_3$) δ 11.82 (bs, 1H, hydroperoxide proton), 8.12 (d, J = 5.6 Hz, 1H), 7.74−7.62 (m, 2H,), 7.53−7.48 (m, 2H), 6.37, (d, J = 5.6 Hz, 1H), 4.03, (s, J_{CH} = 252.0 Hz, 1H); ^{13}C NMR (63 MHz, CD$_3$COCD$_3$) δ 170.2, 152.5, 136.1, 135.7, 130.9, 130.1, 127.4, 124.2, 122.0, 112.2, 85.4,

82.1; IR (KBr, cm^{-1}) 3276, 3117, 2913, 2851, 1748, 1469, 1433, 1337, 1243, 1123, 1075, 935.5. Anal. Calcd for C$_{12}$H$_8$O$_4$: C, 66.69; H, 3.70. Found: C, 66.33; H, 3.66.

3-(2-Ethynylbenzoyl)acrylic Acid (6). To a stirred solution of 140 mg (0.64 mmol) of hydroperoxide **5** in 15 mL of dichloromethane was added 2 mL of saturated sodium bisulfite solution at room temperature (ca. 20 °C). The resulting mixture was stirred for 5 min, while the reaction progress was monitored by means of the peroxide test (KI/HOAc). The mixture was extracted with dichloromethane (2 × 50 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure ca. 20 °C at 15 Torr to afford a light yellow solid (77 mg; 60%): mp 100 °C from dichloromethane−carbon tetrachloride; ^{1}H NMR (250 MHz, CDCl$_3$) δ 10.00 (bs, 1H,), 7.92 (d, J = 15.6 Hz, 1H), 7.70−7.61 (m, 2H), 7.56−7.43 (m, 2H), 6.75 (d, J = 15.6 Hz, 1H), 3.41 (s, 1H); ^{13}C NMR (63 MHz, CDCl$_3$) δ 191.7, 170.7, 141.0, 140.9, 134.5, 132.1, 130.9, 129.1, 129.0 121.0, 84.4, 81.5; IR (KBr, cm^{-1}) 3295.3, 3013, 2684, 1701, 1672, 1590, 1437, 1413, 1307, 1278, 1190, 1014, 920, 749. Anal. Calcd for C$_{12}$H$_8$O$_3$: C, 72.02; H, 3.99. Found: C, 71.89; H, 3.83.

2,3-Biphenylenequinone (12). To a magnetically stirred solution of 350 mg (2.3 mmol) of biphenylene in 20 mL of chloroform were added 12 mg (0.05 mmol) of methyltrioxorhenium, 150 mg (2.5 mmol) of glacial acetic acid, and 0.2 mL (5 mmol) of H$_2$O$_2$ (85%) at room temperature. The mixture was stirred at room temperature for ca. 20 °C for 5 h and extracted with chloroform (2 × 20 mL). The combined extracts were washed with water and dried over magnesium sulfate. The solvent was evaporated at ca. 20 °C and 15 Torr, and the residue was submitted to silica gel (50 g) chromatograph with hexanes−EtOAc as eluent to afford 280 mg of unreacted biphenylene (**3**) and 60.0 mg (0.32 mmol; 83%) of a red-orange solid, mp 210−212 °C identified as 2,3-biphenylenequinone (**12**): ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.72 (s, 4H), 6.62 (s, 2H); ^{13}C NMR (63 MHz, CDCl$_3$) δ 179.5, 156.5, 147.8, 135.2, 124.1, 115.9; IR (KBr, cm^{-1}) 3076, 1642, 1560, 1299, 1243, 1220, 1077, 857.

Dimethyldioxirane Epoxidation of Biphenylene to the Trisepoxide 13. To a magnetically stirred solution of 5 mL (ca. 0.39 mmol) of dimethyldioxirane (DMD) in acetone was added 40.0 mg (0.260 mmol) of biphenylene (**3**), and the resulting mixture was stirred at room temperature (ca. 20 °C) for 24 h, while the reaction progress was monitored by means of the peroxide test (KI/HOAc). After evaporation of the solvent at ca. 20 °C and 15 Torr, the mixture was chromatographed on silica gel (30 g) with hexane−EtOAc (4:1) as eluent to afford 25.0 mg unreacted biphenylene (**3**) and 15.0 mg (97%) triepoxide **13** as colorless solids: mp 205.2−205.8 °C from ether−hexane; ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.50−7.72 (AA′BB′ system, 4H), 3.98 (s, 2H), 3.48 (s, 2H); ^{13}C NMR (63 MHz, CDCl$_3$) δ 144.1, 131.4, 122.4, 68.24, 53.4, 52.9; IR (KBr, cm^{-1}) 3014, 1603, 1485, 1467, 1361, 1324, 1287, 1163, 1135, 1089, 994, 956. Anal. Calcd for C$_{12}$H$_8$O$_3$: C, 72.02; H, 3.99. Found: C, 71.75; H, 4.10.

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