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$[2\pi+2\sigma]$ and $[4\pi+2\sigma]$ Type Cycloaddition Reactions of Furan and Benzofurans with Benzocyclopropene

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Synopsis. Reactions of benzocyclopropene with furan and benzofuran afforded $[2\pi+2\sigma]$-type cycloaddition products, where the furans act as 2π-components and benzocyclopropene acts as a 2σ-component. A similar reaction with 1,3-diphenylisobenzofuran gave a $[4\pi+2\sigma]$-type cycloaddition product using the furan as a 4π-component.

It is known that benzocyclopropene (**1**) is a highly strained and reactive species, which is likely to behave as a 6π-donator in $[6\pi+4\pi]$-type cycloaddition reactions,[1] except a reaction with butadiene, where **1** reacts as a 2σ-donator affording a $[2\pi+2\sigma]$-type cycloadduct among many product mixtures.[1b]

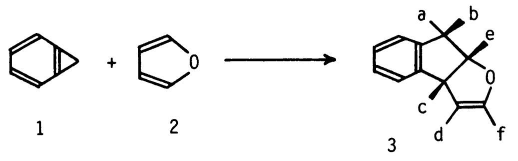
While the addition reactions of **1** with various kinds of olefins have been extensively investigated,[1,2] only a few reactions with heterocyclic partners are known. As one part of our research on the cycloaddition reactions of heterocyclic compounds, we investigated cycloaddition reactions of furan derivatives with **1**.[3] Here, the results of these reactions will be reported.

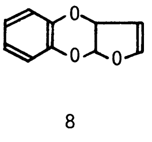
A chloroform solution of furan **2** and an equimolar amount of **1** was allowed to stand at room temperature for 6 days. The separation and purification of the reaction mixture by thin-layer chromatography on silica gel afforded a $[2\pi+2\sigma]$-type cycloadduct **3** in a 39% yield. The reaction of **1** with benzofuran **4**, also gave $[2\pi+2\sigma]$-type cycloadducts **5** in a yield of 25%. On the other hand, the reaction of **1** with 1,3-diphenylisobenzofuran **6** gave a $[4\pi+2\sigma]$-type cycloadduct **7** in a 71% yield.

The structure of **3** was determined on the basis of its spectral, especially ^{1}H NMR spectral properties. The good resemblance of the ^{1}H NMR spectral properties of **3** to those of the analogous compound such as **8** supports the structure of **3**.[4] The orientation of the dihydrofuran moiety in **3** was determined on the basis of the coupling constants in its ^{1}H NMR spectrum as follows. The coupling pattern of the signal of the methine proton H_e shows that the neighbouring protons of H_e are only two methylene protons (H_a and H_b) and a methine proton (H_c). The structure which satisfies the above terms is **3**. Another possible structure such as **9** can not explain the NMR spectral properties. The stereochemistry of **3** was deduced on the basis of the coupling constants in the ^{1}H NMR spectrum as shown in the figure. The structure of **5** was also determined on the basis of its spectral properties, comparing them to those of **3**.

The molecular ion peak in the high-resolution Mass spectrum indicates that **7** is a 1 : 1 adduct of **1** and **6**. The NMR spectrum shows that **7** is an unsymmetrical compound that has geminal protons. The IR spectrum designates that **7** has no carbonyl or hydroxyl groups, showing that the oxygen atom of **7** is an ether oxygen. These considerations lead to the structure shown in the figure.

The reaction is most likely initiated by the cleavage of a cyclopropene bond in a homolytic fashion to give a diradical intermediate **10**, which attacks the furans to produce the cycloadducts via a diradical inter-





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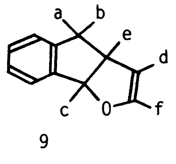

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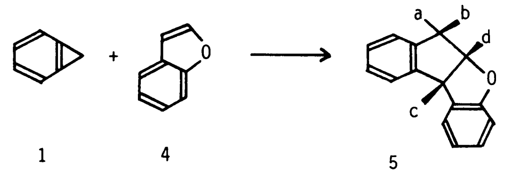

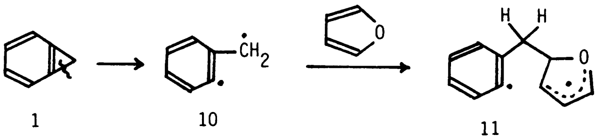

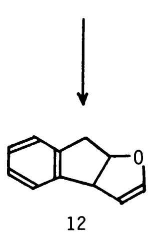

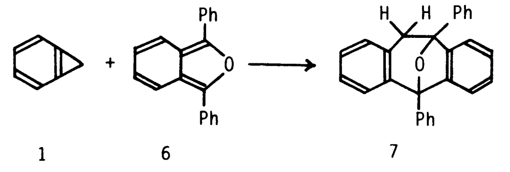

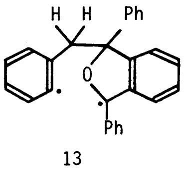

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mediate **11**.[1b)] The stabilization of **11** by the delocalization of the radical electron is considered to determine the orientation of the dihydrofuran moiety in the final cycloadduct **12**. The reaction of **1** with **6** is also considered to proceed via the diradical intermediate **10**, which attacks the 1-position of **6** to produce the benzyl radical-type intermediate **13**. The cyclization of **13** keeping the benzene structure in the isobenzofuran moiety, affords **7**.

The same type of reactions of **1** with pyrrole derivatives such as 1-methyl-, 1-phenyl-, and 1-(methoxycarbonyl)pyrrole resulted in a recovery of the starting materials. The difference between the reactivities of furans and pyrroles are considered to be attributable to the difference in the degree of the aromaticity of these two kinds of compounds. It is known that furans are less aromatic than pyrroles because of a strong electronegativity of oxygen atom comparing to that of nitrogen atom.[5)] Thus, it is cocluded that less aromatic compounds, furans, react with **1**; on the other hand, the more aromatic compounds, pyrroles, are electronically too stable to react with **1**.

Experimental

NMR spectra were measured with Varian XL 200 or Hitachi R-20B spectrometers with tetramethylsilane as an internal standard. IR spectra were measured with DS-701G spectrometer. Mass spectra were measured with Hitachi M-52 or JMS-DX300 spectrometers. Wako gel B5F was used for thin-layer chromatography.

Reaction of 1 with 2. A mixture of **1** (90 mg, 1 mmol) and **2** (70 mg, 1 mmol) in chloroform (0.3 ml) was allowed to stand at room temperature for 6 days. The reaction mixture was separated by thin-layer chromatography on silica gel using benzene as a developing solvent to give an oil **3** (65 mg, 39%, R_f=0.70).

3: Found: *m/z* 158.0711. Calcd for $C_{11}H_{10}O$: M, 158.0732. MS *m/z* (rel intensity) 158 (M^+, 87), 129 (100), 83 (87). IR (neat) 3050, 2920, 1615, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.16 (dd, H_a), 3.37 (dd, H_b), 4.36 (ddd, H_c), 5.09 (dd, H_d), 5.31 (ddd, H_e), 6.24 (dd, H_f), 7.2 (m, 4H). Coupling constants in Hz: J_{ab}=18, J_{ae}=2, J_{be}=7, J_{cd}=3, J_{ce}=10, J_{cf}=2, J_{df}=3.

Reaction of 1 with 4. A mixture of **1** (50 mg, 0.6 mmol) and **4** (71 mg, 0.6 mmol) in chloroform (0.3 ml) was heated at 50 °C for 40 h. The reaction mixture was separated by thin-layer chromatography on silica gel using petroleum ether (bp 35—60 °C)–chloroform 1:4 as a developing solvent to give an oil **5** (30 mg, 25%, R_f=0.75).

5: Found: *m/z* 208.0873. Calcd for $C_{15}H_{12}O$: M, 208.0888. MS *m/z* (rel intensity) 208 (M^+, 100), 189 (10), 179 (17), 115 (10). IR (neat) 3050, 2920, 1593, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.34 (dd, H_a), 3.49 (dd, H_b), 4.82 (d, H_c), 5.61 (ddd, H_d), 6.8—7.6 (m, 8H). Coupling constants in Hz: J_{ab}=18, J_{ad}=2, J_{bd}=6, J_{cd}=9.

Reaction of 1 with 6. A mixture of **1** (45 mg, 0.5 mmol) and **6** (130 mg, 0.5 mmol) in chloroform (0.3 ml) was allowed to stand at room temperature for 7 days. The reaction mixture was separated by thin-layer chromatography on silica gel using petroleum ether (bp 35—60 °C)–benzene 1:4 as a developing solvent to give an oil **7** (120 mg, 71%, R_f=0.70).

7: Found: *m/z* 360.1502. Calcd for $C_{27}H_{20}O$: M, 360.1514. MS *m/z* (rel intensity) 360 (M^+, 1), 120 (2), 83 (100). IR (neat): 3050, 2920, 1593, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.17 (d, 1H, *J*=17 Hz), 3.75 (d, 1H, *J*=17 Hz), 7.0—7.8 (m, 18H).

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