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HIGH-PRESSURE CYCLOADDITION REACTION OF 1,3-DIPHENYLISOBENZOFURAN WITH 6,6-DIPHENYLFULVENE

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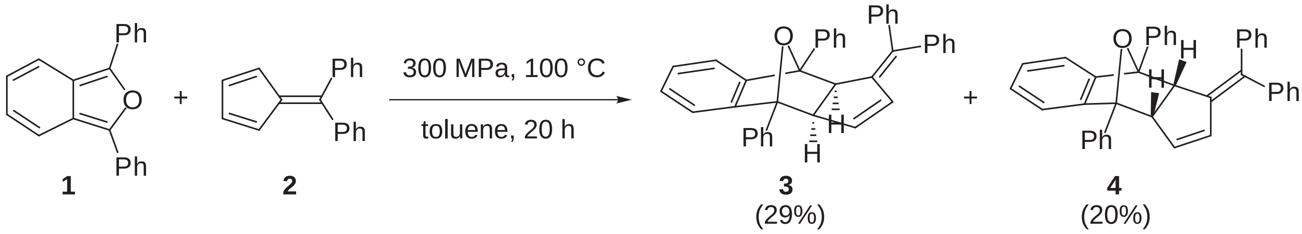
Abstract—High-pressure cycloaddition reaction of 1,3-diphenylisobenzofuran with 6,6-diphenylfulvene gave *exo*- and *endo*-[4+2]π cycloadducts in 29 and 20% yields, respectively. The structures of *exo*- and *endo*-[4+2]π cycloadducts were elucidated by X-Ray crystallographic analysis, the latter of which included a benzene molecule.

Previously we reported the cycloaddition reactions of isobenzofuran with tropones,[1] azulenequinones,[2] and fulvenes.[3] Isobenzofuran reacted at 160 °C with 6,6-diphenylfulvene to give two *endo*-[4+2]π cycloadducts, an *endo*-1:1 adduct and an *endo*-*anti*-*endo*-1:2 adduct. As observed in the reaction of 6,6-dimethylfulvene with cyclopentadiene, the fulvene reacted as a 2π component to give a [2+4] adduct.[4] This has been explained by considering the next-lowest unoccupied orbital (NLUMO) of the fulvene. On the other hand, the reaction of 6,6-dimethylfulvene with isobenzofuran gave an *endo*-[6+4] cycloadduct at room temperature, which was obtained by the interaction between the LUMO of the fulvene and the HOMO of isobenzofuran.[5] As an extention of the study about the reaction of isobenzofuran with fulvenes, we now report the reaction of 1,3-diphenylisobenzofuran with 6,6-diphenylfulvene under high-pressure conditions and the crystal structure of the products.

Dedicated to Professor Yuichi Kanaoka on the occasion of his 75th birthday.

When a xylene solution of 1,3-diphenylisobenzofuran and 6,6-diphenylfulvene was refluxed, it caused no change and resulted in the recovery of starting materials. Under high-pressure (300 MPa) and heating at 100 °C in toluene solution for 20 h, a reaction occurred to give two crystalline products (**3**, 29% and **4**, 20%). Obviously, the absence of the [4+6]π and *endo*-*anti*-*endo*-1:2 cycloaddition process, which were observed in the reactions of isobenzofuran with 6,6-disubstituted fulvenes, may be a result of the steric hindrance of diphenyl group.



From the chemical shifts of the methine protons, the structures[6] of **3** and **4** were assigned to be an *exo*- and an *endo*-[4+2] cycloadduct; the methine protons of *endo*-adduct (**4**) should appear at lower magnetic fields than those of *exo*-adduct (**3**) because of the anisotropy of the oxygen atom on the bridge. Finally the structures of **3**[7] and **4**[8] were confirmed by X-Ray crystallographic analysis as shwon in Figure 1.

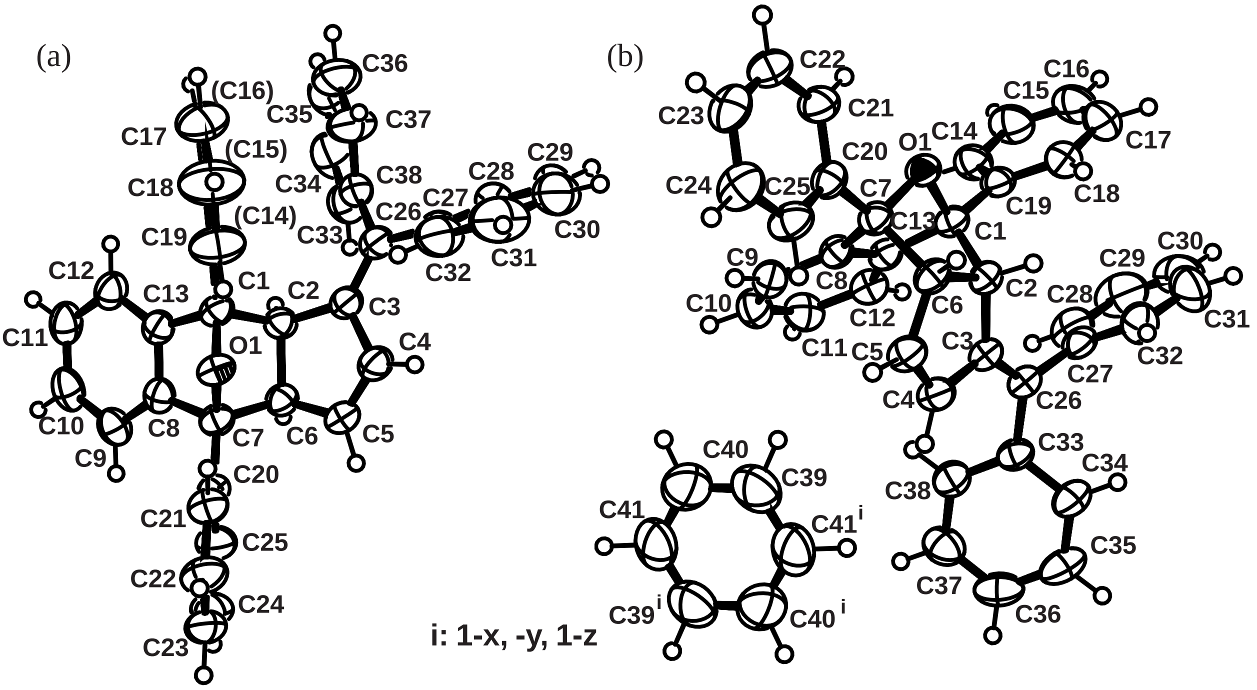


Figure 1. ORTEP drawings of (a) **3** and (b) **4**·0.5(C_6H_6).

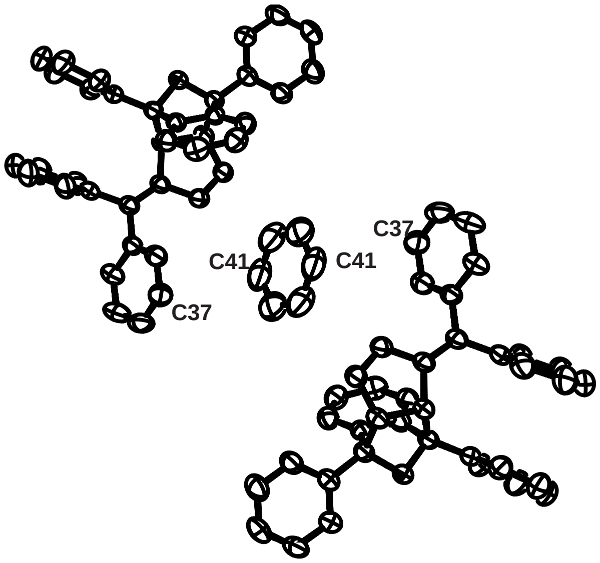


Figure 2. Packing structure of **4**.

The dihedral angle between the cyclopentene ring (defined by C2, C3, C4, C5, and C6) and the benzene ring of a 7-oxabenzobicyclo[2.2.1]nonene system (defined by C8, C9, C10, C11, C12, and C13) is 8.6° for **3** and 129.5° for **4**, respectively. Interestingly, the crystals of **4** formed a 1:2-complex with a benzene molecule as shown in Figure 2. Two *endo*-cycloadducts included a benzene molecule through an intermolecular π-π interaction; the distance between the benzene ring of **4** and the benzene molecule is 3.455 Å for C37···C41^{i} [i: 1-x, -y, 1-z], which is within the range (3.3–3.8 Å)[9] of intermolecular π-π interaction.

In the high-pressure cycloaddition reaction of **1** with **2**, the *exo*-adduct was a main product. This is parallel to the result observed in the high-pressure cycloaddition reaction of 3,4-dimethoxybenzofuran with 1,4-benzoquinone, where *exo*- and *endo*-adducts were obtained and the amount of the *exo*-isomer increased at higher pressure conditions.[10]

In conclusion, high-pressure cycloaddition reaction of 1,3-diphenylisobenzofuran with 6,6-diphenylfulvene afforded *exo*- and *endo*-[4+2]π cycloadducts. *endo*-Cycloadduct (**4**) formed the inclusion complex with benzene in the crystals, which suggested that *endo*-cycloadduct (**4**) may be used as a host molecule for organic solvents.

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6. Synthetic details and physical properties will be reported elsewhere. **3**: colorless crystals, mp 208–209 °C, ^{1}H NMR ($CDCl_3$) δ=3.88 (1H, *ddd*, *J*=7.0, 2.2, 1.1 Hz), 4.34 (1H, *d*, *J*=7.0 Hz), 5.70 (1H, *dd*, *J*=5.7, 1.1 Hz), 6.28 (1H, *dd*, *J*=5.7, 2.2 Hz), 6.73 (2H, *dd*, *J*=7.3, 1.1 Hz), 6.89 (2H, *dd*, *J*=8.0, 1.1 Hz), 7.05-7.24 (12H, *m*), 7.34-7.39 (2H, *m*), 7.50 (2H, *t*, *J*=8.0 Hz), and 7.68 (2H, *d*, *J*=8.0 Hz); Anal. Calcd for $C_{38}H_{28}O$: C, 91.17; H, 5.64. Found: C, 90.87; H, 5.71. **4**: colorless crystals, mp 168–169 °C, ^{1}H NMR ($CDCl_3$) δ=4.26 (1H, *ddd*, *J*=7.7, 2.2, 1.1 Hz), 4.89 (1H, *d*, *J*=7.7 Hz), 5.80 (1H, *dd*, *J*=5.7, 1.1 Hz), 5.85 (1H, *dd*, *J*=5.7, 2.2 Hz), 6.70 (2H, *d*, *J*=6.6 Hz), 6.89 (1H, *d*, *J*=7.4 Hz), 6.96-6.99 (7H, *m*), 7.06-7.14 (4H, *m*), 7.25 (1H, *t*, *J*=7.4 Hz), 7.36-7.38 (4H, *m*), 7.42 (2H, *t*, *J*=7.4 Hz), 7.52 (1H, *d*, *J*=7.4 Hz), and 7.62 (2H, *d*, *J*=7.4 Hz); Anal. Calcd for $C_{38}H_{28}O$: C, 91.17; H, 5.64. Found: C, 91.03; H, 5.81.
7. Crystal data for **3**: $C_{38}H_{28}O$, M_r=500.60, monoclinic, $P2_1/c$, a=14.0213 (8) Å, b=9.2710 (5) Å, c=20.9452 (12) Å, β=91.767 (3)°, V=2721.4 (3) Å^3, Z=4, D_x=1.222 Mg m^{-3}, T=296 K, R=0.0701, refinement on F^2 (SHELXL97),[11] $wR(F^2)$=0.2027.
8. Crystal data for **4**: $C_{38}H_{28}O \cdot 0.5(C_6H_6)$, M_r=539.66, triclinic, $P\overline{1}$, a =11.7036 (8) Å, b =11.8455 (11) Å, c =11.1343 (9) Å, α =97.796 (4)°, β =91.799 (3)°, γ =73.403 (4)°, V =1465.6 (2) Å^3, Z =2, D_x =1.223 Mgm^{-3}, T=296 K, R=0.0633, refinement on F^2 (SHELXL97),[11] $wR(F^2)$=0.1964.
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