February, 1990] *Bull. Chem. Soc. Jpn., 63, 395—400 (1990)*

The Addition of 1,3-Diphenylisobenzofuran to Cyclooctatetraene and to Dimethyl Cyclooctatetraene-1,2-dicarboxylate. The Benzene Ring as a Dienophile in an Intramolecular Diels–Alder Reaction

Katsuhiro SAITO,* Yoichi OMURA, Etsuro MAEKAWA, and Paul G. GASSMAN†
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
†Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

(Received July 4, 1989)

The reaction of cyclooctatetraene with 1,3-diphenylisobenzofuran afforded two kinds of 1 : 1 [2π+4π]-cycloadducts, a cage-type 1 : 1 cycloadduct and two classes of 1 : 2 cycloadducts. The cage-type compound was formed from one of the [2π+4π]-cycloadducts via an unprecedented second [2π+4π]-cycloaddition reaction in which the double bond of the benzene moiety acted as a dienophile. A similar reaction with dimethyl cyclooctatetraene-1,2-dicarboxylate gave a 1 : 1 [2π+4π]-cycloadduct and a 1 : 2 cycloadduct. No cage-type compound was formed.

Cyclooctatetraene (**1**) is known to react either as a dienophile (2π-component)[1] or as a diene (4π-component) in thermal [2π+4π]-cycloaddition reactions.[2] Many papers have been published which discuss cycloaddition reactions in which **1** acts as a diene; the mechanisms of these reactions have been discussed in detail. However, examples of cycloadditions in which **1** acts as a dienophile are relatively few in number.

Thermal cycloaddition reactions of benzene have been researched extensively, and it is known that benzene acts only as a diene in the Diels–Alder reaction.[3] We are unaware of any thermal [2π+4π]-cycloadditions in which the benzene moiety reacts as a dienophile.

As a part of our research on the cycloaddition reactions of cyclic olefins,[4] we have studied the addition reactions of two cyclooctatetraenes with 1,3-diphenylisobenzofuran (**2**) and have found novel reactions in which **1** and the benzene moiety both behave as dienophiles. We now wish to report on the details of this investigation.[4]

Results and Discussion

A solution of **1** and an equimolar amount of **2** in benzene was heated at 200 °C for 72 h in a sealed ampule. A chromatographic separation of the components of the reaction mixture on silica gel afforded two adducts **3** and **4** in 28 and 11% yield respectively. In the same reaction, but under milder conditions (100 °C for 26 h), **3** and three different cycloaddition

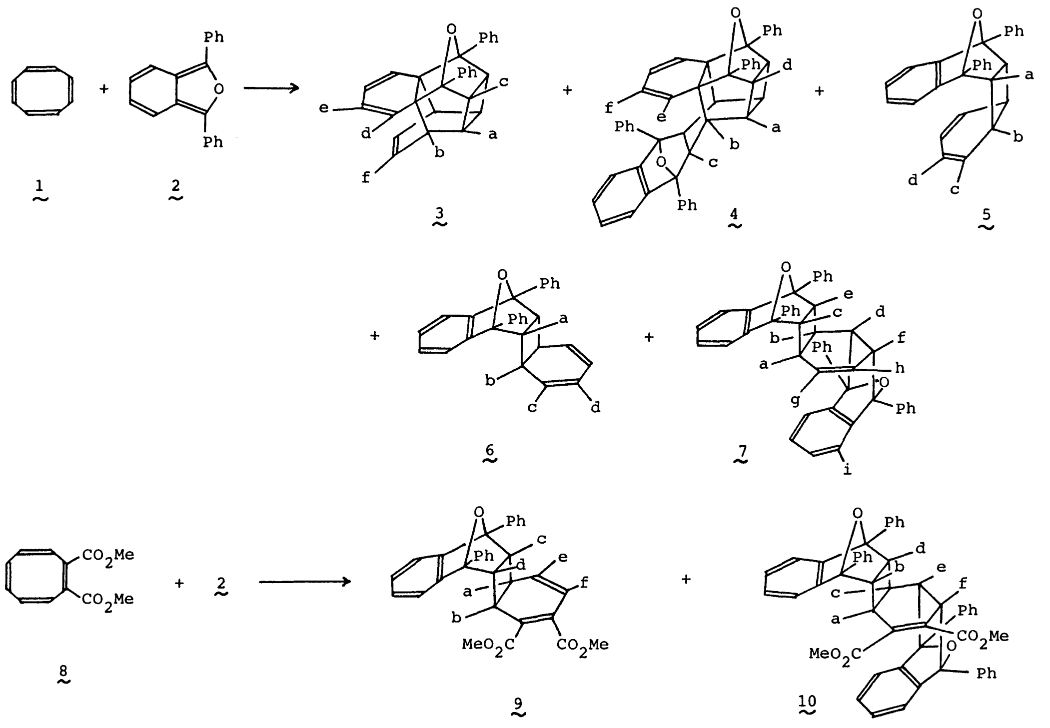


Fig. 1.

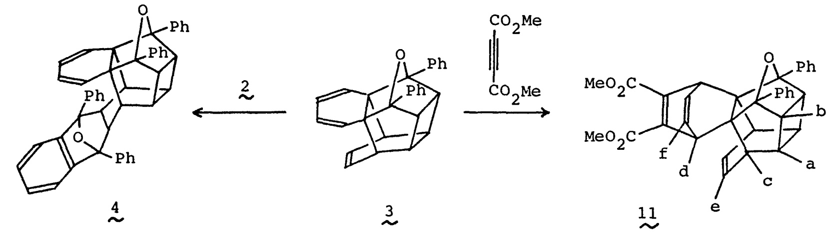


Fig. 2.

products **5**, **6**, and **7** were obtained in 3, 4, 6, and 30% yield, respectively. Dimethyl cyclooctatetraene-1,2-dicarboxylate (**8**) gave two cycloadducts **9** and **10** in 9 and 12% yields, respectively, in a related sequence of reactions.

The elemental analyses and the molecular ion peaks in the mass spectra showed that **3**, **5**, and **6** were 1 : 1 adducts of **1** and **2**, while **4** and **7** were proven to be 1 : 2 adducts of **1** and **2**, respectively.

The structure of **3** was determined mainly on the basis of its NMR spectral properties through the use of double and triple resonance techniques, as well as from the following facts. The reaction of **3** with **2** and dimethyl acetylenedicarboxylate gave 1 : 1 adducts **4** and **11**, respectively,[5] indicating that **3** has an isolated olefinic bond and a conjugated diene system. The structure of **3** was finally confirmed by single-crystal X-ray analysis.[6,7]

The structure of **7** was determined mainly on the basis of its NMR spectral properties, employing double and triple resonance techniques. The structure of **7** was further supported by a comparison of the ^1H NMR spectral data of **7** with those of the analogous compound **12**, whose structure had been determined earlier by single-crystal X-ray analysis.[8]

The structures of **5** and **6** were determined on the basis of their NMR spectral properties and by their chemical behaviors. Upon heating at 130 °C, **5** gave **3** and **2** in 22 and 19% yields, respectively, accompanied by the recovery of **5** in 31% yield. The formation of **2** is the result of a retro-Diels–Alder reaction of **5**, and the formation of **3** is the result of an intramolecular $[2\pi+4\pi]$-cycloaddition reaction.

The reaction of **6** with three molar equivalents of **2** in xylene at 110 °C for 3 h afforded **7** in quantitative yield. The reversible nature of this cycloaddition reaction was demonstrated when **7** was maintained at 140 °C for 24 h in xylene. At the end of this period, the reaction mixture contained **6** and unreacted **7** in yields of 57 and 40%. Under these reaction conditions, no interconversion between **5** and **6** was observed.

The structure of **10** was deduced on the basis of the NMR spectral properties observed using double and

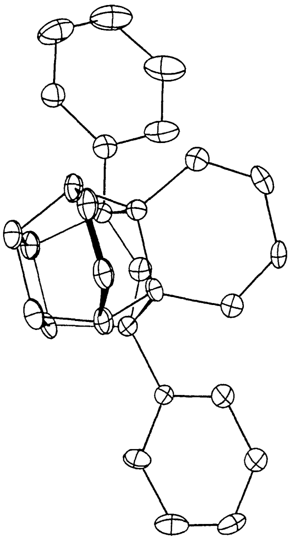
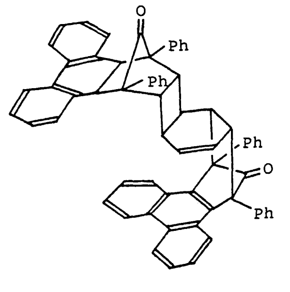


Fig. 3.



12

Fig. 4.

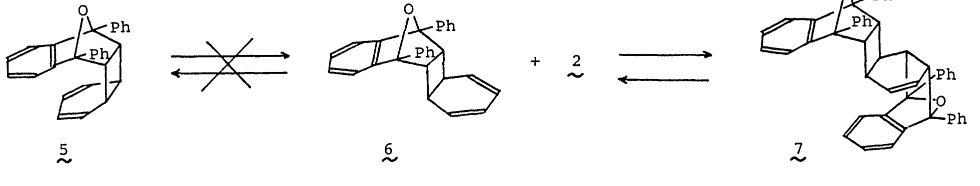


Fig. 5.

triple resonance techniques and by a close comparison of the ^{1}H NMR data of **10** with those of **7**. The structure of **9** was also deduced mainly on the basis of its ^{1}H NMR spectral properties and by the observation that heating of a chloroform solution of **10** at 60 °C for 6 h afforded **9** in 21% yield accompanied by the recovery of **10** (57%).

It is of interest to explore the series of reactions described above from a mechanistic point of view. As indicated, a [$2\pi+4\pi$]-cycloaddition of **1** to **2** formed primary products **5** and **6**. 1,3-Diphenylisobenzofuran (**2**) is known to be a powerful 4π component in Diels-Alder reactions. As a result, it is not surprising that **2** acted as the diene and that the role of **1** was changed from its usual role of diene to that of the dienophile (2π component). Similar conclusions can be drawn for the cycloaddition reaction of **8** to **2** to form **9**. Again, **2** played the role of the 4π component while **8** took on the unusual role of the 2π component in the Diels-Alder reaction.[9)]

The cyclohexadiene moiety of both **6** and **9** underwent a second reaction with **2** to form 2:1 adducts **7** and **10**, respectively. Interestingly, **2** again served as the 4π component while the 1,3-cyclohexadiene system provided the 2π component.

The formation of **3** from **5** is considered to have proceeded via an intramolecular [$2\pi+4\pi$]-cycloaddition where the benzene moiety acted as a 2π component. Benzene is known to react as a 4π component in thermal [$2\pi+4\pi$]-cycloaddition reactions with acetylene and ethylene derivatives to give barrelene and dihydrobarrelene derivatives, respectively.[3)] It is also well-known that benzene reacts as a 2π component in photoinduced [$2\pi+2\pi$]-cycloaddition reactions with acetylenes to give cyclooctatetraenes[10a)] and reacts as a 4π component in photoinduced [$4\pi+4\pi$]-cycloaddition reactions with conjugated dienes to give bicyclo[4.2.2]decatrienes.[10b)]

However, we are unaware of any reactions in which the benzene ring acts as a 2π component in thermal [$2\pi+4\pi$]-cycloaddition reactions. We believe that the isomerization of **5** to **3** constitutes the first example of a thermal [$2\pi+4\pi$]-cycloaddition reaction where benzene reacts as a 2π component. The forced proximity of the 2p-orbitals of the benzene moiety to the 2p-orbitals of the ends of the butadiene moiety in **5** is considered to account for the reaction.[11)]

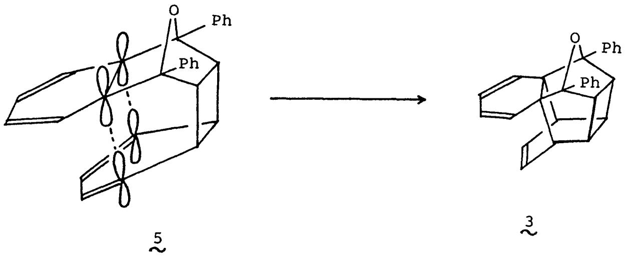


Fig. 6.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were measured with a Varian HA 100 or a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard. UV and IR spectra were measured with Hitachi 220A and DS-701G spectrometers, respectively. Mass spectra were measured with a Hitachi M-52 spectrometer. Wakogel C-200 and Wakogel B5F were used for column and thin-layer chromatography, respectively.

Reaction of Cyclooctatetraene (1) with 1,3-Diphenylisobenzofuran (2) at 200 °C. A mixture of **1** (0.83 g, 80 mmol) and **2** (2.18 g, 81 mmol) in benzene (25 ml) was heated at 200 °C for 72 h in a sealed ampule. After evaporation of the solvent the tarry residue was chromatographed on a silica-gel column to give crystalline **3** (844 mg, 28%) by elution with petroleum ether-benzene (1:1) and crystalline **4** (582 mg, 11%) by elution with petroleum ether-benzene (2:3). Recrystallization of **3** and **4** from ethyl acetate gave pure samples with the properties described.

3: mp 217—218 °C. Found: C, 89.85; H, 5.84%. Calcd for $C_{28}H_{22}O$: C, 89.84; H, 5.88%. MS *m/z* (rel intensity): 374 (M^+, 13), 269 (6), 220 (100), 191 (7), 156 (65). UV (EtOH): 275 nm (log ε, 3.51). IR (KBr): 3050, 2910, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.57 (2H, m, H_a), 3.01 (2H, m, H_b), 3.20 (2H, m, H_c), 4.59 (2H, m, H_d), 5.50 (2H, m, H_e), 6.27 (2H, m, H_f), 7.2—7.5 (10H, m, Ph).

4: mp>300 °C. Found: C, 89.18; H, 5.48%. Calcd for $C_{48}H_{36}O_2$: C, 89.41; H, 5.63%. MS *m/z* (rel intensity): 346 (2), 283 (3), 270 (12), 220 (100), 185 (4). UV (EtOH): 265 nm (log ε, 3.70), 272 (3.71), 284 (3.65). IR (KBr): 3030, 2920, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.03 (2H, m, H_a), 2.38 (2H, m, H_b), 2.42 (2H, m, H_c), 2.76 (2H, m, H_d), 4.46 (2H, m, H_e), 5.67 (2H, m, H_f), 6.9—7.7 (24H, m, Ph).

Reaction of Cyclooctatetraene (1) with 1,3-Diphenylisobenzofuran (2) at 100 °C. A solution of **1** (1.00 g, 96 mmol) and **2** (2.60 g, 96 mmol) in benzene (30 ml) was heated at 100 °C for 26 h in a sealed ampule. After evaporation of the solvent the tarry material was chromatographed on a silica-gel column to give crystalline **5** (144 mg, 3.9%) by elution with petroleum ether-benzene (7:3), crystalline **6** (206 mg, 5.6%), crystalline **3** (114 mg, 3.1%), and crystalline **7** (1900 mg, 30%) eluted in this order with petroleum ether-benzene (6:4). These crystalline compounds were purified by recrystallization from ethyl acetate and had the following properties.

5: mp 173—174 °C. Found: C, 89.79; H, 5.93%. Calcd for $C_{28}H_{22}O$: C, 89.84; H, 5.88%. MS *m/z* (rel intensity): 374 (M^+, 3.2), 296 (8.1), 283 (17.5), 270 (100), 241 (11), 164 (16). UV (EtOH): 266 nm (log ε, 3.70), 273 (3.72). IR (KBr): 3030, 2910, 1605 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.67 (2H, m, H_a), 3.03 (2H, m, H_b), 5.48 (4H, m, H_c, H_d), 6.9—7.7 (14H, Ph).

6: mp 176—177 °C. Found: C, 89.72; H, 6.16%. Calcd for $C_{28}H_{22}O$: C, 89.84; H, 5.88%. MS *m/z* (rel intensity): 374 (M^+, 0.5), 356 (3), 296 (23), 283 (37), 270 (100), 241 (20), 165 (23). UV (EtOH): 266 (log ε, 3.66), 273 (3.43). IR (KBr): 3030, 2910, 1605 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.08 (2H, m, H_a), 3.31 (2H, m, H_b), 5.71 (4H, m, H_c, H_d), 6.9—7.6 (14H, m, Ph).

7: mp 203—204 °C. Found: C, 89.42; H, 5.55%. Calcd for $C_{48}H_{36}O_2$: C, 89.41; H, 5.63%. MS *m/z* (rel intensity): 296 (2.4), 283 (28), 270 (100), 241 (40), 155 (96). UV (EtOH): 265 nm (log ε, 3.73), 272 (3.50). IR (KBr): 3030, 2910, 1605 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=0.77 (m, H$_a$), 1.37 (m, H$_b$), 2.66 (m, H$_c$), 3.04 (m, H$_d$), 3.20 (m, H$_e$), 3.53 (m, H$_f$), 5.48 (m, H$_g$), 5.80 (m, H$_h$), 6.48 (m, H$_i$), 6.8—7.7 (27H, m, Ph). Coupling constants (Hz): J_{ab}=9, J_{ac}=4, J_{ag}=3, J_{ah}=2, J_{ce}=10, J_{be}=6, J_{df}=10, J_{fh}=4, J_{gh}=11.

Reaction of Dimethyl Cyclooctatetraene-1,2-dicarboxylate (8) with 1,3-Diphenylisobenzofuran (2). A mixture of **8** (2.00 g, 91 mmol) and **2** (2.45 g, 91 mmol) in xylene (25 ml) was heated at 185 °C for 20 h. After evaporation of the solvent, the tarry residue was chromatographed on a silica-gel column to give crystalline **9** (386 mg, 8.7%) by elution with petroleum ether-benzene (2 : 3) and crystalline **10** (822 mg, 12%) by elution with benzene. Recrystallization from ethanol and benzene gave pure **9** and **10**, respectively, with the following properties.

9: mp 137—138 °C. Found: C, 78.30; H, 5.51%. Calcd for $C_{32}H_{26}O_5$: C, 78.35; H, 5.34%. MS *m/z* (rel intensity): 490 (M$^+$, 0.7), 283 (10.3), 270 (100), 220 (32), 160 (60). UV (EtOH): 250 nm (log ε, sh, 3.30). IR (KBr): 3030, 2970, 1730 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=2.86 (m, H$_a$), 2.95 (m, H$_b$), 3.12 (m, H$_c$), 3.34 (m, H$_d$), 3.48 (3H, s), 3.70 (3H, s), 5.71 (dd, H$_e$), 6.10 (d, H$_f$), 7.0—7.8 (14H, m, Ph). Coupling constants (Hz): J_{ab}=2, J_{ac}=3, J_{ae}=4, J_{bd}=3, J_{cd}=7, J_{ef}=10.

10: mp 125—126 °C. Found: C, 81.89; H, 5.31%. Calcd for $C_{52}H_{40}O_6$: C, 82.08; H, 5.30%. MS *m/z* (rel intensity): 296 (1), 270 (100), 241 (20), 193 (7), 135 (19). UV (EtOH): 243 nm (log ε, 3.70). IR (KBr): 3030, 2980, 1730 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.46 (m, H$_a$), 2.29 (m, H$_b$), 2.64 (m, H$_c$), 2.98 (m, H$_d$), 3.12 (3H, s), 3.22 (d, H$_e$), 3.48 (3H, s), 4.18 (d, H$_f$), 6.8—8.0 (28H, m, Ph). Coupling constants (Hz): J_{ab}=8, J_{ac}=4, J_{bd}=8, J_{cd}=6, J_{ef}=10.

Reaction of the 1 : 1 Adduct 3 with Dimethyl Acetylenedicarboxylate. A solution of **3** (200 mg, 0.54 mmol) and dimethyl acetylenedicarboxylate (310 mg, 2.18 mmol) in benzene (2.5 ml) was heated at 120 °C for 68 h. After evaporation of the solvent the residue was chromatographed on a silica-gel thin-layer plate using benzene as the developing solvent to give crystalline **11** (194 mg, 70%, R_f=0.25).

11: mp 268—270 °C. Found: C, 79.00; H, 5.38%. Calcd for $C_{34}H_{28}O_5$: C, 79.05; H, 5.46%. MS *m/z* (rel intensity): 516 (M$^+$, 20), 322 (35), 270 (29), 220 (100), 163 (40). UV (EtOH): 244 nm (log ε, 4.57). IR (KBr): 3030, 2980, 1710 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=2.43 (2H, m, H$_a$), 2.90 (2H, m, H$_b$), 3.14 (2H, m, H$_c$), 3.26 (2H, m, H$_d$), 6.12 (2H, m, H$_e$), 6.23 (2H, m, H$_f$), 7.2—7.3 (10H, m, Ph).

Reaction of the 1 : 1 Adduct 3 with 1,3-Diphenylisobenzofuran (2). A solution of **3** (57 mg, 0.15 mmol) and **2** (41 mg, 0.15 mmol) in benzene (5 ml) was heated at 170 °C for 24 h. After evaporation of the solvent the residue was subjected to thin-layer chromatography on silica gel using cyclohexane-benzene (3 : 2) as a developing solvent to give crystals of recovered **3** (43 mg, 75%, R_f=0.6) and crystalline **4** (9 mg, 9.2%, R_f=0.5).

Thermal Isomerization of the 1 : 1 Adduct 5 to 3. A solution of **5** (45 mg, 0.12 mmol) in benzene (0.5 ml) was heated at 130 °C for 27 h and the reaction mixture was chromatographed on a silica-gel thin-layer plate using petroleum ether-benzene (1 : 1) as the developing solvent to give crystalline **2** (6 mg, 19%, R_f=0.85), recovered **5** (14 mg, 31%, R_f=0.70) and crystalline **3** (10 mg, 22%, R_f=0.35).

Thermal Decomposition of the 1 : 2 Adduct 7. A solution of **7** (1.50 g) in xylene (10 ml) was heated at 140 °C for 24 h. After evaporation of the solvent, the residue was chromatographed on a silica-gel column to give crystalline **6** (496 mg, 57%) by elution with petroleum ether-benzene (1 : 1) and recovered **7** (588 mg), by elution with petroleum ether-benzene (1 : 4).

Reaction of the 1 : 1 Adduct 6 with 1,3-Diphenylisobenzofuran (2). A mixture of **6** (40 mg, 0.11 mmol) and **2** (80 mg, 0.30 mmol) in xylene (0.3 ml) was heated at 110 °C for 3 h. After evaporation of the solvent, the residue was separated with thin-layer chromatography on silica gel using petroleum ether-benzene (1 : 2) as a developing solvent to give crystalline **7** (51 mg, 74%, R_f=0.35).

Thermal Decomposition of the 1 : 2 Adduct 10. A solution of **10** (470 mg, 0.62 mmol) in benzene (35 ml) was heated at 80 °C for 11 h. After evaporation of the solvent, the residue was subjected to thin-layer chromatography on silica gel using benzene-ether (9 : 1) as the developing solvent to give crystalline **2** (114 mg, 68%, R_f=0.85), recovered **10** (76 mg, R_f=0.75), and crystalline **9** (239 mg, 79%, R_f=0.70).

The authors are indebted to Dr. Michael McGuiggan and Professor Louis H. Pignolet for their help in the X-ray study. PGG is indebted to the National Science Foundation for a grant which partially supported this investigation and for grant CHE77-2805, which aided in the purchase of an Enraf-Nonius X-ray diffractometer.

References

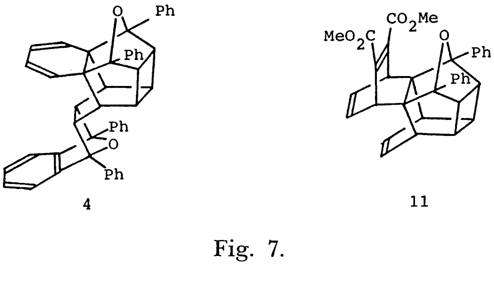
1) R. Huisgen and M. Christl, *Angew. Chem.*, **79**, 471 (1967); M. Christl and R. Huisgen, *Tetrahedron Lett.*, **1968**, 5299; G. Bianchi, R. Gondolfi, and P. Grunanger, *Tetrahedron*, **26**, 5113 (1970); M. Yasuda, K. Harano, and K. Kanematsu, *Tetrahedron Lett.*, **21**, 627 (1980); *J. Am. Chem. Soc.*, **103**, 3120 (1981).

2) H. Isaksen and J. P. Snyder, *Tetrahedron Lett.*, **1977**, 889; W. G. Dauben, G. T. Rivers, R. J. Twieg, and W. T. Zimmerman, *J. Org. Chem.*, **41**, 887 (1976); G. Mehta and A. Srikrishna, *Tetrahedron Lett.*, **1979**, 3187; W. Adam and G. Klug, *ibid.*, **23**, 3155 (1982).

3) E. Ciganek, *Tetrahedron Lett.*, **1967**, 3321; G. C. Johnson and R. G. Bergman, *ibid.*, **1979**, 2093.

4) K. Saito, Y. Omura, and T. Mukai, *Chem. Lett.*, **1980**, 349; K. Saito, Y. Omura, E. Maekawa, and P. G. Gassman, *Tetrahedron Lett.*, **25**, 2573 (1984); K. Saito, Y. Omura, and T. Mukai, *Bull. Chem. Soc. Jpn.*, **58**, 1663 (1985); K. Saito and H. Ishihara, *ibid.*, **58**, 2664 (1985) and **59**, 1095 (1986); K. Saito, T. Mukai, and S. Iida, *ibid.*, **59**, 2485 (1986).

5) The stereochemistries of **4** and **11** are hard to be decided. However, considering the stereorepulsions in the transition states in the reactions to form these adducts, the possible stereochemistries of **4** and **11** may be thought to be



4 11

Fig. 7.

those shown in Fig. 7.[7]

6) The colorless crystals of $C_{28}H_{22}O$ belong to the monoclinic space group $P2_1/n$-C_{2h}^5. The measured cell constants, a=7.634(4), b=22.184(3), c=11.719(2) Å and β=104.07(2)°, gave a calculated density of 1.292 g cm^3 for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf-Nonius CAD4 Diffractometer by using a variable rate ω-2θ scan technique and graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). After Lorentz-polarization corrections, 2099 of 3749 unique reflections (56%) with 2θ=0—50° were obsereved for [$F_o \geq 2\sigma(F_o)^2$]. A combination of direct methods and difference Fourier synthesis was used to locate all non-hydrogen atoms. The non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares analysis. The hydrogen atoms were included at idealized positions with fixed isotropic thermal parameters. The final wR was 0.043. All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SPD programs described by B. A. Frentz, "Computing in Crystallography," ed by H. Schenck, R. Olthof-Hazekamp, H. van Konigweld, and G. S. Bassie, Delft University Press, Delft, Holland (1978), pp. 64—71.

7) The fact that **3** reacts with **2** only at the olefinic part to form **4**, but not at the diene part can be explained as follows. The transition state for the diene-part-adduct is considered to be **13**, whereas the transition state for **4** is **14**. The stereorepulsion between the phenyl group of **2** and the oxygen atom of **3** in the transition state **13** is considered to destabilize **13** comparing to **14**.

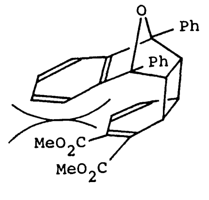
8) M. Yasuda, K. Harano, and K. Kanematsu, *J. Am. Chem. Soc.*, **103**, 3120 (1981).

9) The steric repulsion between the benzene moiety and the ester group is considered to explain the absence of the syn-adduct **9′** corresponding to **5**.

10) a) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, **1963**, 695; A. H. A. Tinnemans and D. C. Neckers, *Tetrahedron Lett.*, **1978**, 1713. b) N. C. Yang and J. Libman, *ibid.*, **1973**, 1409; N. C. Yang, C. V. Neywick, and K. Srinivasachar, *ibid.*, **1975**, 4313; N. C. Yang, J. Masvovi, and W. Chiang, *J. Am. Chem. Soc.*, **101**, 6465 (1979).

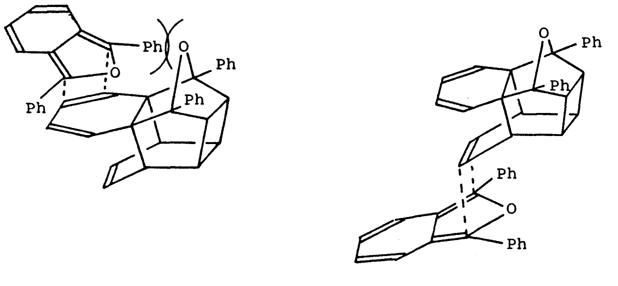
11) The configurations of the primary products (**5**, **6**) are all endo-configurations. This fact seems to show that these addition reactions proceed through the endo-type transition state (**15**) where cyclooctatetraene reacts in the cyclooctatetrarene-form (**1**). The secondary orbital interaction can stabilize **15**. The endo-type intermediate (**16**) which is formed through **15** can give each final products **5** and **6** via a valence tautomerisation.

In the case of that cyclooctatetraene reacts as the valence tautomer, bicyclo[4.2.0]cyclooctatriene (**1b**), four kinds of transition states (**17**, **18**, **20**, and **22**) are considered to be



9′

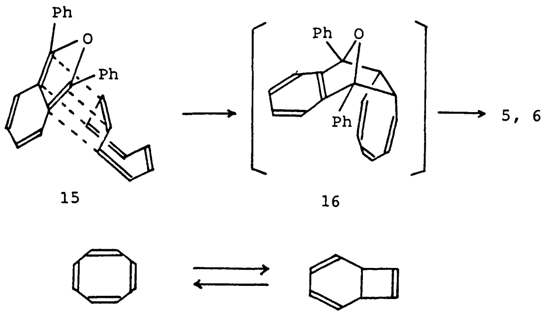
Fig. 9.



13

14

Fig. 8.



15

16

1

1b

Fig. 10.

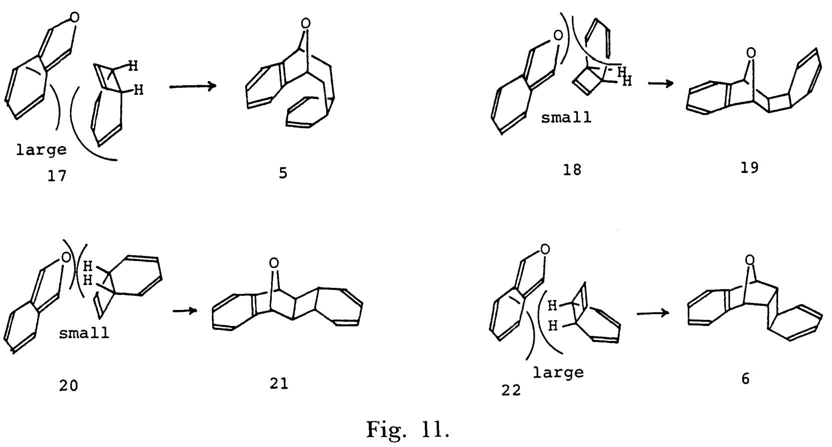


Fig. 11.

possible. In all of these transition states, no secondary orbital interactions exist resulting that the steric stability controls the reaction as follws. The steric repulsion between the cyclohexadiene moieties of **2** and **1b** in **17** should be larger than the repulsion between the cyclohexadiene part of **1b** and the ether oxygen atom of **2** in the transition form **18**. This consideration leads to the conclusion that the adduct **19** should be formed rather than **5**.

The same relation can be applied to the transition states **20** and **22**. The repulsion between the brigde-head protons of **1b** and the ether oxygen atom of **2** in **20** should be smaller than the repulsion between the bridge-head protons of **1b** and the cyclohexadiene part of **2** in **22**, resulting that the adduct **21** should be afforded rather than **6**. These consideration seems to support the endo-addition mechanism via the cyclooctatetraene form.