

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

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The reaction of cyclooctatetraene with 1,3-diphenylisobenzofuran afforded two kinds of 1:1 $[2\pi+4\pi]$ -cycloadducts, a cage-type 1:1 cycloadduct and two classes of 1:2 cycloadducts. The cage-type compound was formed from one of the $[2\pi+4\pi]$ -cycloadducts via an unprecedented second $[2\pi+4\pi]$ -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 $[2\pi+4\pi]$ -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 $[2\pi+4\pi]$ -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 $[2\pi+4\pi]$ -cycloadditions in which the benzene moiety reacts as a dienophile.

As a part of our research on the cycloaddition reac-

tions 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

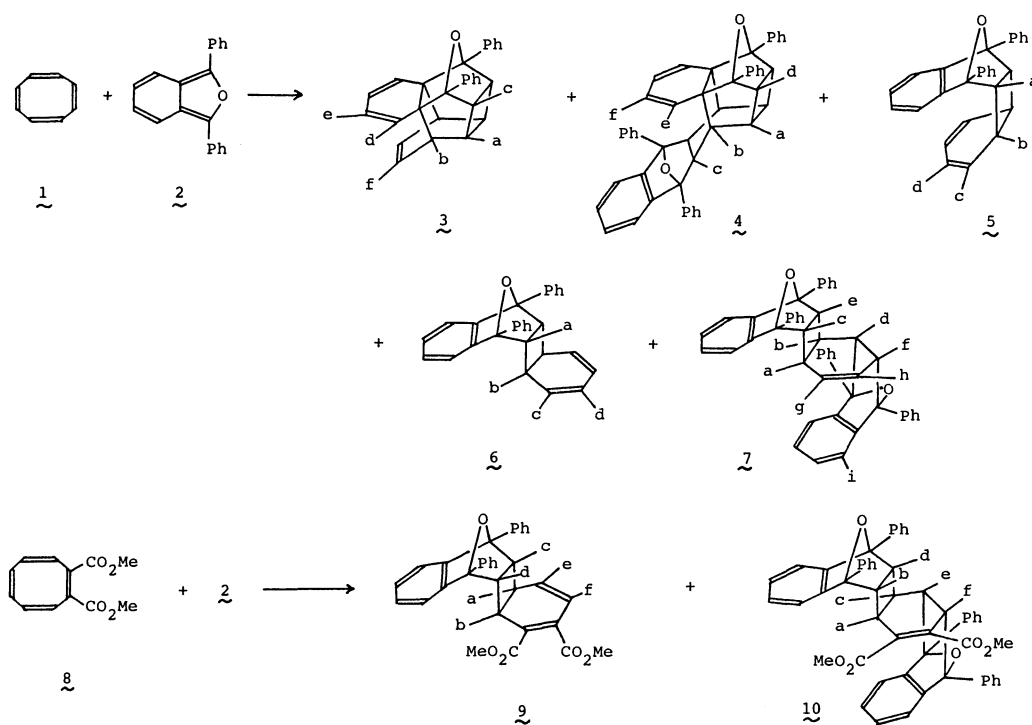


Fig. 1.

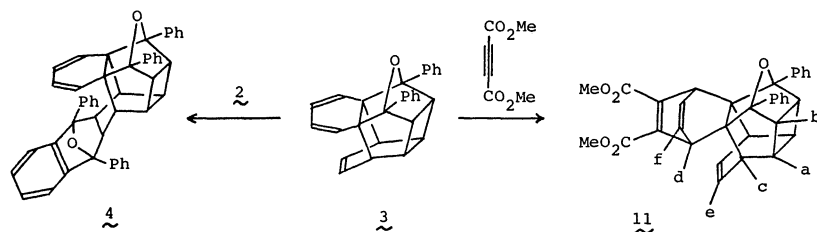


Fig. 2.

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

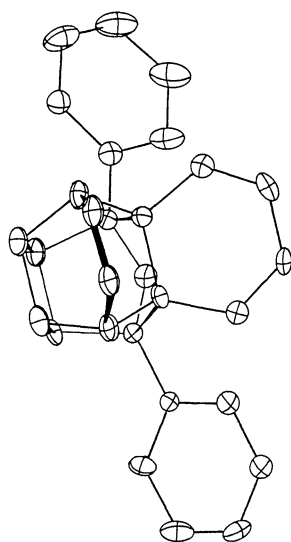


Fig. 3.

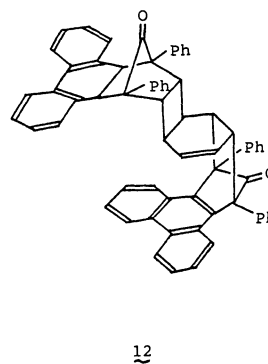


Fig. 4.

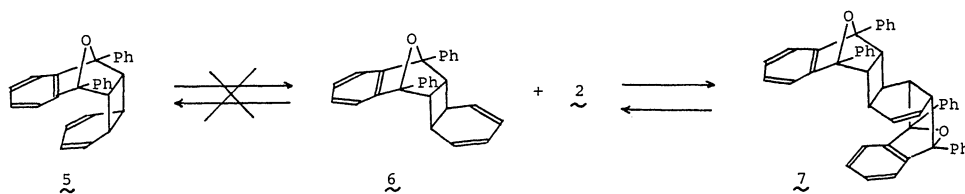


Fig. 5.

triple resonance techniques and by a close comparison of the ^1H NMR data of **10** with those of **7**. The structure of **9** was also deduced mainly on the basis of its ^1H 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⁾

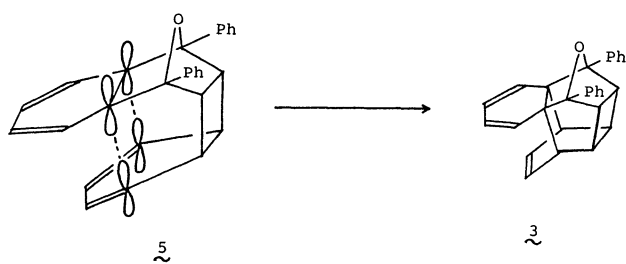


Fig. 6.

Experimental

All melting points are uncorrected. ^1H 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 $217\text{--}218^\circ\text{C}$. Found: C, 89.85; H, 5.84%. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}$: 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 ($\log \epsilon$, 3.51). IR (KBr): 3050, 2910, 1600 cm^{-1} . ^1H NMR (CDCl_3): $\delta=2.57$ (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 $>300^\circ\text{C}$. Found: C, 89.18; H, 5.48%. Calcd for $\text{C}_{48}\text{H}_{36}\text{O}_2$: 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 ($\log \epsilon$, 3.70), 272 (3.71), 284 (3.65). IR (KBr): 3030, 2920, 1600 cm^{-1} . ^1H NMR (CDCl_3): $\delta=2.03$ (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 $173\text{--}174^\circ\text{C}$. Found: C, 89.79; H, 5.93%. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}$: 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 ($\log \epsilon$, 3.70), 273 (3.72). IR (KBr): 3030, 2910, 1605 cm^{-1} . ^1H NMR (CDCl_3): $\delta=2.67$ (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 $176\text{--}177^\circ\text{C}$. Found: C, 89.72; H, 6.16%. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}$: 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 ($\log \epsilon$, 3.66), 273 (3.43). IR (KBr): 3030, 2910, 1605 cm^{-1} . ^1H NMR (CDCl_3): $\delta=2.08$ (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 $203\text{--}204^\circ\text{C}$. Found: C, 89.42; H, 5.55%. Calcd for $\text{C}_{48}\text{H}_{36}\text{O}_2$: 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 ($\log \epsilon$, 3.73), 272 (3.50). IR (KBr): 3030, 2910, 1605 cm^{-1} .

cm^{-1} . $^1\text{H NMR}$ (CDCl_3): $\delta=0.77$ (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): $J_{ab}=9$, $J_{ac}=4$, $J_{ag}=3$, $J_{ah}=2$, $J_{ce}=10$, $J_{bc}=6$, $J_{df}=10$, $J_{fh}=4$, $J_{gh}=11$.

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 $\text{C}_{32}\text{H}_{26}\text{O}_5$: 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 ($\log \epsilon$, sh, 3.30). IR (KBr): 3030, 2970, 1730 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): $\delta=2.86$ (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 $\text{C}_{52}\text{H}_{40}\text{O}_6$: 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 ($\log \epsilon$, 3.70). IR (KBr): 3030, 2980, 1730 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): $\delta=1.46$ (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 $\text{C}_{34}\text{H}_{28}\text{O}_5$: 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 ($\log \epsilon$, 4.57). IR (KBr): 3030, 2980, 1710 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): $\delta=2.43$ (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 chromatog-

raphed 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%, $R_f=0.70$).

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- 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

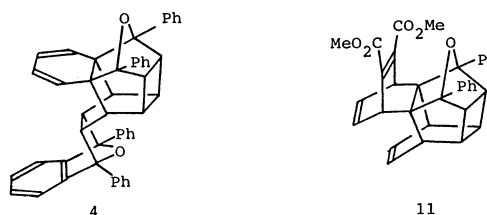


Fig. 7.

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 $\beta=104.07(2)^\circ$, 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 ($\lambda=0.71069$ Å). After Lorentz-polarization corrections, 2099 of 3749 unique reflections (56%) with $2\theta=0-50^\circ$ were observed 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. Frenz, "Computing in Crystallography," ed by H. Schenck, R. Olthoff-Hazekamp, H. van Konigsweld, 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).

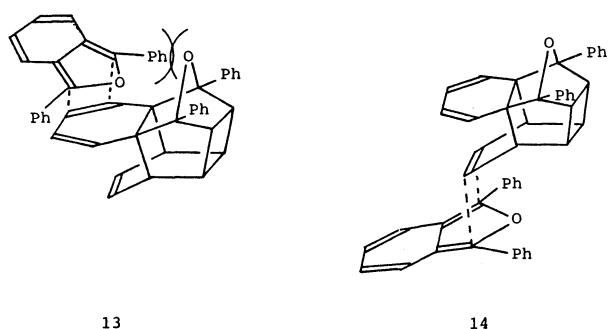


Fig. 8.

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 cyclooctatetraene-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

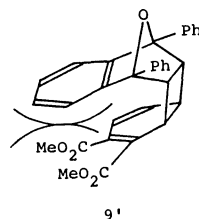


Fig. 9.

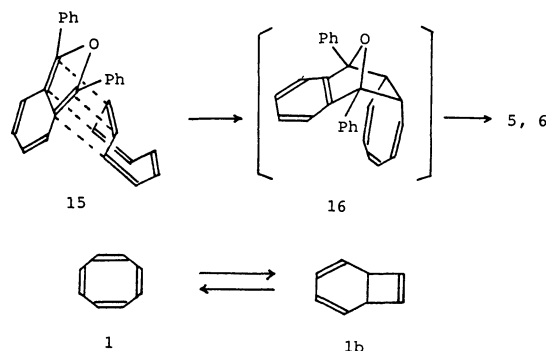


Fig. 10.

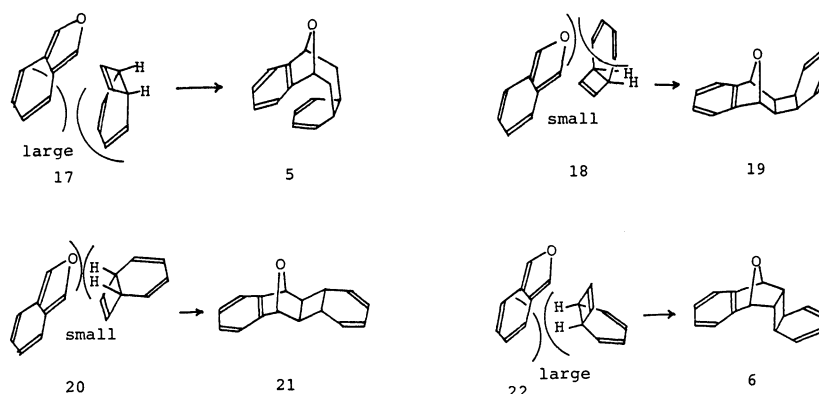


Fig. 11.

possible. In all of these transition states, no secondary orbital interactions exist resulting that the steric stability controls the reaction as follows. 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 bridge-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 considerations seem to support the endo-addition mechanism via the cyclooctatetraene form.
