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Decompositions of Tropone Tosylhydrazone Sodium Salt in the Presence of Cyclopentadienone Derivatives. [4+2]-Type Cycloaddition Reactions of Cycloheptatrienylidene or 1,2,4,6-Cycloheptatetraene with Cyclopentadienone Derivatives

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Tropone tosylhydrazone sodium salt, the precursor of the cyclic conjugated carbene (cycloheptatrienylidene), was decomposed in the presence of various cyclopentadienone derivatives to give endo- and exo-[4+2]-type adducts and benzotropylidene derivatives. The product ratios between the endo-[4+2]-type adducts and the exo-[4+2]-type adducts are considered to suggest that these addition reactions proceed *via* a cyclic conjugated allene (1,2,4,6-cycloheptatetraene), which is a valence-bond isomer of cycloheptatrienylidene. Upon heating, the [4+2]-type adducts gave the benzotropylidene derivatives *via* decarbonylation reactions followed by 1,5-hydrogen shifts.

Recently, medium-sized ring-conjugated allenes are attracting the attention of chemists from the viewpoint of the addition reactions and the molecular rearrangements of the allenes.[1] Allenes are twisted molecules with rectlinear three-carbon atoms. Consequently, medium-sized ring allenes are considered to have a considerable amount of strain energy. It is known that three-membered ring-cyclic carbenes, cyclopropylidenes, rearrange to allenes *via* ring-opening processes.[2]

Cycloheptatrienylidene (**2**), which is generated by the thermolysis of a tropone tosylhydrazone sodium salt (**1**) (accompanied by nitrogen gas and sodium *p*-toluenesulfinate (**3**)), is known to be a nucleophilic singlet carbene because of a contribution of the 6 π-electrons aromatic structure (**2b**).[3] Actually, **2**, preferentially reacts with electron-deficient double bonds,[3c] and adds to maleonitrile and fumalonitrile with stereospecificity.[3d]

Recently, a possibility of an isomerization of the carbene (**2**) and a medium-sized ring-conjugated allene, 1,2,4,6-cycloheptatetraene (**4**), was pointed out and a number of reports have been published concerning this isomerization.[3,4]

As a part of our research on the reactivity of **2**,[3f] we studied addition reactions of **2** with various cyclopentadienone derivatives and obtained a result which suggests that **2** is rearranged to **4**. Here we wish to report on this result.

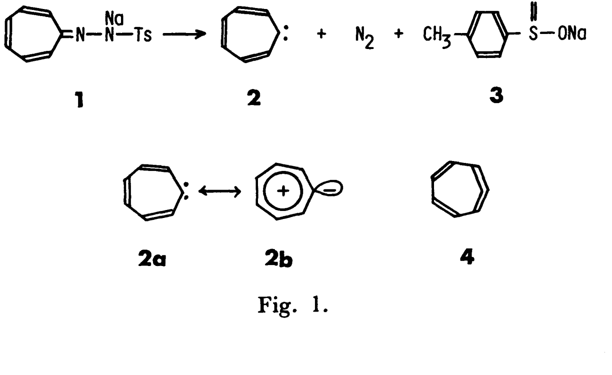


Fig. 1.

Results and Discussion

When tropone tosylhydrazone sodium salt (**1**) was allowed to decompose in anhydrous diglyme at 95 °C for 3 h in the presence of 2 mole equivalents of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**5**), an endo-[4+2]-type adduct (**6**), exo-[4+2]-type adduct (**7**), and a benzotropylidene derivative (**8**) were afforded in 16, 2, and 9% yields, respectively. Under similar conditions, **1** was allowed to decompose in the presence of tetracyclone (**9**) to give an exo-[4+2]-type adduct (**10**) and two kinds of benzotropylidene derivatives (**11** and **12**)[3e] in 8, 6, and 10% yields, respectively. The same type of reaction of **1** with phencyclone (**13**) afforded an endo-[4+2]-type adduct (**14**) in a 17% yield. The analogous reaction of **1** with a cyclopentadienone derivative (**15**) gave a benzo-tropylidene derivative (**16**) in a 24% yield.

The endo- and exo-[4+2]-type adducts (**6** and **7**) gave the benzotropylidene derivative (**8**) in 79 and 80% yields upon heating at 105 °C for 180 h and 120 h, respectively. No interconversion between **6** and **7** was observed. The two kinds of benzotropylidene derivatives **11** and **12** were afforded by pyrolysis of exo-[4+2]-type adduct (**10**) at 100 °C for 80 h in 17 and 69% yields, respectively. On the other hand, upon heating at 100 °C for 2h, endo-[4+2]-type adduct (**14**) rearranged in a 80% yield to exo-[4+2]-type adduct (**17**), which gave a benzotropylidene derivative (**18**) in a 85% yield upon heating at 150 °C for 100 h. Considering this thermal isomerization of **14** to **17**, it seems not to be unreasonable to think that the exo-[4+2]-type adduct (**10**) is afforded by a thermal isomerization of the initially formed endo-[4+2]-type adduct, which corresponds to the endo-[4+2]-type adduct **6**.

The structures of the products were determined on

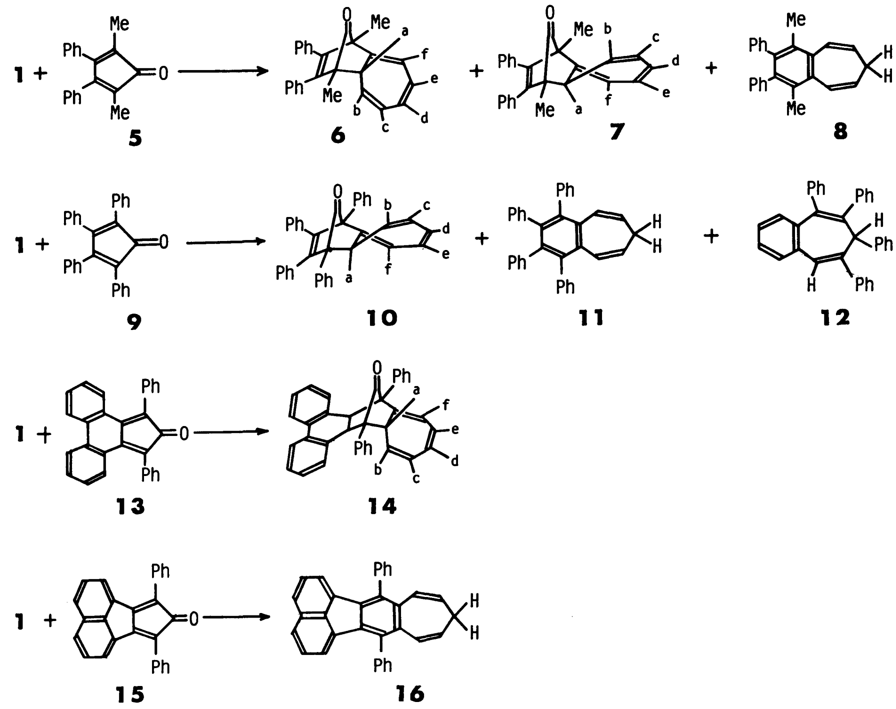


Fig. 2.

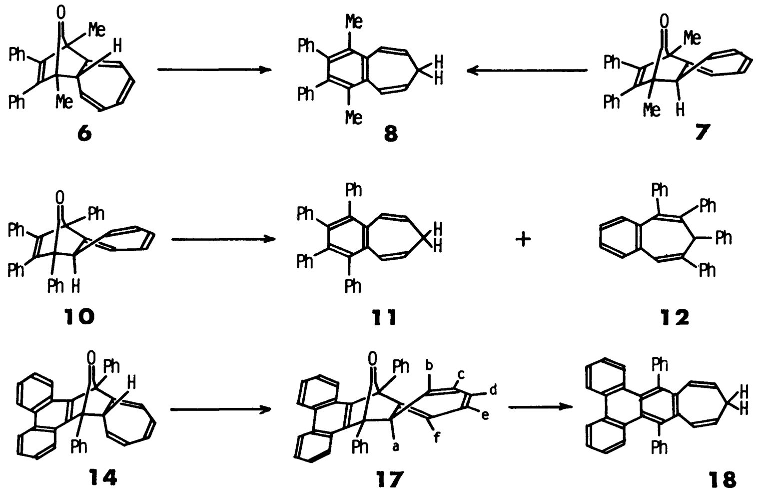


Fig. 3.

Table. NMR Data of the [4+2]-type adducts

Adducts		H_a (d)	H_b (dd)	H_c (m)	H_d, H_e, H_f (m)	Me (s)	Ph (m)	J_{ab}	J_{ac}
		Chemical shifts (δ, ppm) in $CDCl_3$						Coupling constants (Hz)	
Endo	6	3.12	4.91	6.1—6.7 (4H)		1.30, 1.48	7.0—7.5 (10H)	4	10
	14	4.35	4.73	5.70	6.3—6.7 (3H)		7.0—8.7 (18H)	4	10
	20[3f)]	3.68	4.75	5.85	6.1—6.5 (3H)		7.0—7.8 (14H)	4	10
Exo	7	2.30	5.21	6.2—6.9 (4H)			7.0—7.5 (10H)	4	10
	10	2.63	5.12	6.2—6.8 (4H)			7.0—7.8 (20H)	4	10
	17	2.30	5.43	6.2—6.9 (4H)			7.0—8.7 (18H)	4	10
	21[3f)]	2.60	5.15	6.05	6.3—6.7 (3H)		7.0—7.8 (14H)	4	10
	22[3f)]	2.46	4.63	5.86	6.2—6.5 (3H)		7.0—7.5 (8H)	4	10

the basis of their physical properties and confirmed by comparisons of these properties to those of the analogous compounds, such as **19**, **20**, and **21**.[3f,5,6] The stereochemistries of the endo- and exo-[4+2]-type adducts were determined by comparisons of the chemical shifts of the methine protons (H_a) of the adducts to those of the corresponding methine protons (H_a) of the endo-compound (**19**), exo-compound (**20**), and the compound **21**, whose methine proton corresponds to the methine proton of the exo-[4+2]-type adducts. The NMR signal of the methine proton (H_a) of **14** appears at a low field (4.35 ppm) compairing to that of **6** (3.12 ppm) because of a paramagnetic anisotropic effect of the phenyl group attached to the carbon atom adjacent to the carbon atom bearing the methine proton (H_a). The benzo-tropylidene derivatives **11** and **12** are compounds from the literature.[3e]

The formation mechanism of the [4+2]-type adducts (**6**, **7**, **10**, and **14**) via the carbene, cycloheptatrienylidene (**2**), requires a multistep reaction through the tropylium cation intermediate (**22**) (Path A). According to the Dreiding model there is no obvious difference between the steric repulsions in the formations of the endo-[4+2]-type adducts (**6** and **14**) and the exo-[4+2]-type adducts (**7** and **10**) from the corresponding intermediates (**22**). The fairly large difference between the yields of the endo-[4+2]-type adduct (**6**, 16%) and the exo-[4+2]-type adduct (**7**, 2%), and the preferential formation of the endo-[4+2]-type adduct (**14**, 17%) would suggest that the reaction does not proceed via the intermediate (**22**).[7]

The major formation of the endo-[4+2]-type adducts, which contain no less strain energies than those of the exo-[4+2]-type adducts suggests the contribution of a stabilization effect of a secondary orbital interaction in the transition state of Diels-Alder type addition reaction *via* the allene, 1,2,4,6-cycloheptatetraene (**4**) (Path B).[8] Cyclopentadienone derivatives are well known to be reactive enophiles in Diels-Alder type addition reactions.[5d,9] Oda has reported that a cyclic conjugated allene derivative reacted with an enophile, diphenylisobenzofuran, to give endo- and exo-[4+2]-type adducts in a yield ratio of 5:1, though without defining the stereochemistry of the adducts.[10]

As mentioned above, it is hard to conclude whether cycloheptatrienylidene (**2**) or 1,2,4,6-cycloheptatetraene (**4**) is involved in the reactions, but the allene mechanism (Path B), which indicates the isomerization of **2** to **4** seems to be plausible.

The benzotropylidene derivative (**8**, **11**, **16**, and **18**) are considered to be formed by the thermally allowed 1,5-hydrogen shift[7] of the intermediate (**23**), which is afforded by a decarbonylation reactions of the corresponding [4+2]-type adducts (**6**, **7**, **10**, and **17**).

Experimental

All the melting points are uncorrected. Mass, UV, and IR spectra were measured with the Hitachi M-52, Hitachi 220A, and DS 701 G spectrometers, respectively. NMR spectra were measured with a Hitachi R-20B or a Varian XL 200 spectrometers with tetramethylsilane as an internal standard. Wako gel C-200 and Wako gel B-5F were used for column and thin-layer chromatography, respectively. Diglyme was dried over Molecular Sieves 3A 1/16.

Reaction of 1 with 5. A mixture of **1** (23.84 g, 80 mmol), dimer of **5** (41.60 g, 160 mmol), and anhydrous diglyme (400 ml) was heated at 95 °C for 3 h. After evolution of nitrogen gas had ceased (1800 ml, *ca.* 100%), the gray powder of **3** (14.30 g, *ca.* 100%) was removed by filtration. The filtrate was extracted with ether, washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give a mixture of crystals and an oil, which was chromatographed on silica gel to yield colorless crystals of **8** (2.45 g, 9%) by pet ether-benzene 9:1, colorless crystals of **6** (4.50 g, 16%) by pet ether-benzene 8:2, a colorless oil of **7** (0.64 g, 2%) by pet ether-benzene 7:3, and crystals of recovered dimer of **5** (3.91 g) by pet ether-benzene 3:7. The crystals of **6** and **8** were purified by

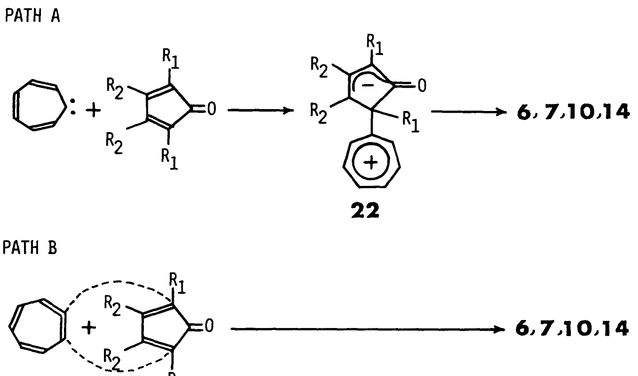
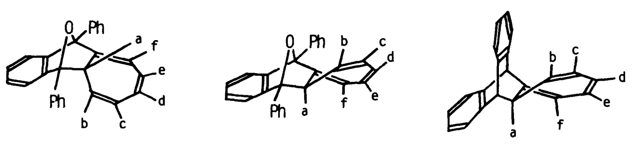
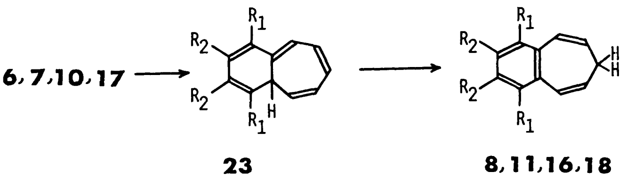


Fig. 5.



19 **20** **21**

Fig. 4.



23 **8,11,16,18**

Fig. 6.

recrystallization from benzene and ethanol, respectively, and the oil of **7** was purified by thin-layer chromatography on silica gel using pet ether-benzene 9:1 as a developing solvent (R_f=0.61). 6: Mp; 158—159 °C. Found: C, 89.37; H, 6.55%. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33%. Mass *m/z* (rel intensity): 350 (M^+, 4), 323 (50), 308 (100), 246 (10). UV (EtOH): 260 nm (log ε, 4.27). IR (KBr): 3030, 1780, 1600 cm^{-1}. **7**: Found: C, 88.08; H, 6.25%. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33%. Mass *m/z* (rel intensity): 350 (M^+, 11), 307 (100), 229 (11), 215 (6). UV (EtOH): 257 nm (log ε, 4.24). IR (neat): 3030, 1780, 1600 cm^{-1}. **8**: Mp 223—224 °C. Found: C, 92.90; H, 6.73%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%. Mass *m/z* (rel intensity): 322 (M^+, 28), 321 (100), 308 (52), 293 (9). UV (EtOH): 253 nm (log ε, 4.36). IR (KBr): 3030, 1600 cm^{-1}. NMR ($CDCl_3$) δ (ppm)=2.12 (s, 6H), 2.32 (t, 2H, *J*=7 Hz), 6.02 (m, 2H), 6.51 (m, 2H), 7.0—7.5 (m, 10H).

Reaction of 1 with 9. A mixture of **1** (23.84 g, 80 mmol), **9** (51.52 g, 160 mmol) and anhydrous diglyme (400 ml) was heated at 95 °C for 3 h to evolve nitrogen gas (1800 ml, *ca.* 100%). After separation of the gray powder of **3** (14.30 g, *ca.* 100%) by filtration, the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of recovered **9** (37.11 g) were separated by filtration, and the filtrate was chromatographed on silica gel to yield colorless crystals of **12** (3.46 g, 10%), **11** (1.97 g, 6%), and **10** (2.34 g, 8%), in this order by pet ether-benzene 8:2. The crystals of **10** were further purified by recrystallization from benzene. **10**: Mp 190—191 °C. Found: C, 90.92; H, 5.41%. Calcd for $C_{36}H_{26}O$: C, 91.11; H, 5.52%. Mass *m/z* (rel intensity): 446 (M^+, 100), 369 (20), 291 (21). UV (EtOH): 253 nm (log ε, 4.18). IR (KBr): 3030, 1790, 1600 cm^{-1}.

Reaction of 1 with 13. A mixture of **1** (8.88 g, 30 mmol), **13**, (22.92 g, 60 mmol) and anhydrous diglyme (150 ml) was heated at 95 °C for 2 h to evolve nitrogen gas (600 ml, 90%). After separation of the gray powder of **3** (4.65 g, 87%) by filtration, the filtrate was treated as usual to yield a mixture of crystals and an oil. The crystals of recovered **13** (19.56 g) were separated by filtration and the filtrate was chromatographed on silica gel to give colorless crystals of **14** (2.41 g, 17%) by pet ether-benzene 5:5. The crystals of **14** were further purified by recrystallization from ethyl acetate. **14**: Mp 216—217 °C. Found: C, 91.21; H, 5.06%. Calcd for $C_{36}H_{24}O$: C, 91.27; H, 5.25%. Mass *m/z* (rel intensity): 472 (M^+, 20), 444 (100), 377 (25), 353 (15). UV (EtOH): 257 nm (log ε, 4.57). IR (KBr): 3030, 1785, 1600 cm^{-1}.

Reaction of 1 with 15. A mixture of **1** (8.88 g, 30 mmol), **15** (21.26 g, 60 mmol) and anhydrous diglyme (150 ml) was heated at 95 °C for 2 h to evolve nitrogen gas (650 ml, 97%). After separation of the gray powder of **3** (5.07 g, 95%) by filtration, the filtrate was treated as usual to give a mixture of crystals and an oil. The crystals of recovered **15** (19.89 g) were separated by filtration and the filtrate was chromatographed on silica gel to yield colorless crystals of **16** (1.57 g, 24%) by pet ether-benzene 1:1. Recrystallization from ethyl acetate gave pure crystals of **16**. **16**: Mp 254—256 °C. Found: C, 94.37; H, 5.03%. Calcd for $C_{33}H_{22}$: C, 94.70; H, 5.30%. Mass *m/z* (rel intensity): 418 (M^+, 100), 341 (22), 326 (18). UV (EtOH): 247 nm (log ε, 4.28). IR (KBr): 3030, 1600 cm^{-1}. NMR ($CDCl_3$) δ (ppm)=2.40(t, 2H, *J*=7 Hz), 5.81 (m, 2H), 6.43 (m, 2H), 7.1—7.9 (m, 16H).

Thermal Reaction of 6 to Form 8. A solution of **6** (760 mg) in toluene (7.5 ml) was heated at 105 °C for 180 h. After evaporation of the solvent on a rotary evaporator, the residue was thin-layer chromatographed on silica gel using pet ether-benzene 8:2 as a developing solvent to give colorless crystals of **8** (550 mg, 79%, R_f=0.78).

Thermal Reaction of 7 to Form 8. A solution of **7** (50 mg) in toluene (1 ml) was heated at 105 °C for 120 h. After evaporation of the solvent, the residue was thin-layer chromatographed on silica gel using pet ether-benzene 8:2 as a developing solvent to give a colorless crystals of **8** (40 mg, 80%).

Thermal Reaction of 10 to Form 11 and 12. A solution of **10** (128 mg) in toluene (3 ml) was heated at 100 °C for 80 h. After evaporation of the solvent, the residue was thin-layer chromatographed on silica gel using pet ether-benzene 8:2 as a developing solvent to give colorless crystals of **12** (90 mg, 69%, R_f=0.81) and colorless crystals of **11** (27 mg, 17%, R_f=0.68).

Thermal Isomerization of 14 to 17. A solution of **14** (40 mg) in deuteriochloroform (0.5 ml) was heated at 100 °C for 2 h in a sealed ampoul. After evaporation of the solvent, the residue was thin-layer chromatographed on silica gel using pet ether-benzene 7:3 as a developing solvent to give a colorless oil of **17** (32 mg, 80%, R_f=0.53). In spite of repeated purification by thin-layer chromatography on silica gel, the analytically pure sample of **17** could not be obtained. **17**: Mass *m/z* (rel intensity): 472 (M^+, 21), 444 (100), 377 (33), 353 (33). UV (EtOH): 254 nm (log ε, 4.50). IR (neat): 3030, 1790, 1605 cm^{-1}.

Thermal Reaction of 17 to Form 18. A solution of **17** (200 mg) in chloroform (5 ml) was heated at 150 °C for 100 h in a sealed ampoul. After evaporation of the solvent, the residue was thin-layer chromatographed on silica gel using pet ether-benzene 1:1 as a developing solvent to give a colorless oil of **18** (170 mg, 85%, R_f=0.83). **18**: Found: C, 94.38; H, 5.43%. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44%. Mass *m/z* (rel intensity): 444 (M^+, 100), 367 (46), 352 (18). UV (EtOH): 293 nm (log ε, 4.05). IR (neat): 3030, 1600 cm^{-1}. NMR ($CDCl_3$) δ (ppm)=2.41 (t, 2H, *J*=7 Hz), 5.73 (m, 2H), 6.42 (m, 2H), 7.0—7.9 (m, 18H).

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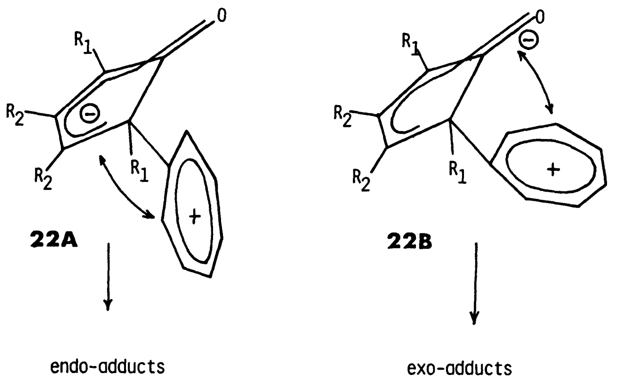

Fig. 7.

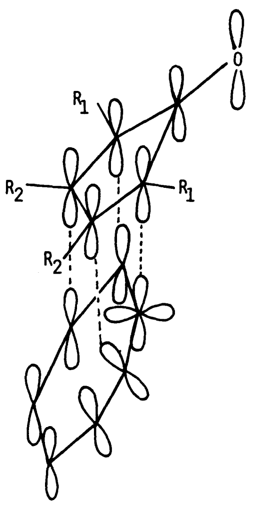

Fig. 8.

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6) T. Mitsuhashi and W. M. Jones have proposed the intermediate corresponding to **10** or its exo-isomer in the reaction of **1** with tetracyclones, though without isolation of them.[3e] We are indebted to Dr. Tsutomu Mitsuhashi of Tokyo University for his Fruitfull suggestions.

7) The preferential formation of the endo-adduct can not be explained by the charge interaction between the anion on the cyclopentadienone moiety and the cation on the cycloheptatriene moiety because of the following reason.[11] Both of the intermediates for the endo- (**22A**) and the exo-adduct (**22B**) are considered to feel almost the same amounts of charge interactions; *i.e.*, the former feels the interaction between the anion mainly on the five-membered ring part of the cyclopentadienone moiety and the cation on the seven-membered ring moiety, on the other hand, the latter feels the interaction between the anion on the carbonyl part of the cyclopentadienone moiety and the cation on the seven-membered ring moiety.

8) The secondary orbital interaction in the transition state is considered to be as shown below. R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); K. Saito, Y. Omura, and T. Mukai, *Bull. Chem. Soc. Jpn.*, **58**, 0000 (1985).

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11) The possibility of the charge interaction was suggested by a referee. We are indebted to the referee for this suggestion.