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Reactions of Tropone Tosylhydrazone Sodium Salt with Anthracene, 1,3-Diphenylisobenzofuran, and Phenylacetylene: [2+2] and [4+2] Type Cycloaddition Reactions of Cycloheptatrienylidene or 1,2,4,6-Cycloheptatetraene

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The reaction of tropone tosylhydrazone sodium salt (**1**) with anthracene gave a [4+2]-type adduct and the reaction of **1** with 1,3-diphenylisobenzofuran afforded *endo*- and *exo*-[4+2]-type adducts as well as a heptafulvene derivative. The reaction of **1** with phenylacetylene yielded a [2+2]-type adduct, which rearranged into 2-phenylindene upon heating. The addition reactions are thought to proceed *via* the allene intermediate, 1,2,4,6-cycloheptatetraene, which is a valence-bond isomer of the carbene intermediate, cycloheptatrienylidene, initially generated by the pyrolysis of **1**. The photoreaction of adduct **3** with a high-pressure mercury lamp afforded a ring-closure product *via* the photobicyclization reaction of the cycloheptatriene moiety of the adduct. Thermal interconversions between the three products of the reaction of **1** with 1,3-diphenylisobenzofuran were investigated.

It is known that tropone tosylhydrazone sodium salt (**1**) generates the carbene, cycloheptatrienylidene (**3a**) accompanied by nitrogen gas and sodium *p*-toluenesulfinate (**2**) by pyrolysis or photolysis.1) Cycloheptatrienylidene is recognized to be a nucleophilic singlet carbene, due to the contribution of a canonical formula (**3b**), which is stabilized by the 6 π-electrons aromatic system.2) Actually, **3a** preferentially reacts with electron-deficient double bonds.2) Recently, Jones *et al.* suggested the possibility of a valence-bond isomerization between the carbene **3a** and an allene, 1,2,4,6-cycloheptatetraene (**3c**), and proved experimentally that **3c** rearranged into **3a**.3) However, the reverse isomerization, **3a** to **3c**, has never been found. We have pyrolyzed **1** in the presence of various olefins and we have evidence which suggests the isomerization of **3a** to **3c**. Here, we wish to report our findings.

Results

When **1** was allowed to react with anthracene (**4**) in anhydrous diglyme at 120 °C for 15 min, the [4+2]-type adduct **5** was afforded in a yield of 21%. The reaction of **1** with 1,3-diphenylisobenzofuran (**6**) under the identical conditions gave two [4+2]-type adducts, **7** and **8**, accompanied by the heptafulvene derivative **9**, in yields of 28, 3, and 4%, respectively. The analogous reaction of **1** with phenylacetylene (**10**) afforded a [2+2]-type adduct **11** and 2-phenyl-1*H*-indene (**12**)4) in yields of 8 and 5%, respectively.

Compound **5** was thermally stable and was recovered quantitatively after heating at 150 °C for 40 h, but turned to polymeric materials upon heating at 180 °C for 20 h. No change was observed when **7** and **8** were kept at 120 °C for 15 min (the conditions of the pyrolysis of **1**), but upon heating at 130 °C for 25 h, **7** gave **8** and **9** in yields of 6 and 42%, respectively, as well as a 30% yield of recovered **7**. Under conditions analogous to the above, **8** afforded **7**, **9**, and recovered **8** in yields of 2, 20, and 68%, respectively. Upon heating at 120 °C for 1 h, **11** rearranged into **12** in a 55% yield. The red oil **9** was unstable and readily decomposed to a resinous material, but catalytic hydrogenation of **9** over palladium–charcoal resulted in the formation of a colorless oil **13** in 96% yield by absorbing 4 molar equivalents of hydrogen.

The irradiation of a methanol solution of **5** using a high-pressure mercury lamp afforded the ring-closure product **14** in a yield of 88%.

The structures of **5**, **7**, and **8** were deduced on the basis of their physical properties and confirmed by a comparison of these properties with those of analogous compounds.5) The stereochemistries of **7** (*endo*-adduct) and **8** (*exo*-adduct) were deduced on the basis of the following arguments. According to Dreiding models, H_a of **8** (δ 2.60) and H_b of **7** (δ 4.75) are expected to appear in a higher field in the NMR spectra compared to H_a of **7** (δ 3.68) and H_b of **8** (δ 5.15), because of the diamagnetic anisotropic effects from the *o*-disubstituted benzene moiety. Furthermore, the chemical shifts of H_a of **7** (δ 3.68) and **8** (δ 2.60) are

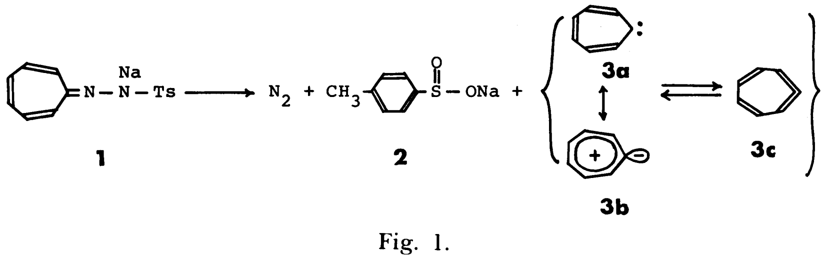

Fig. 1.

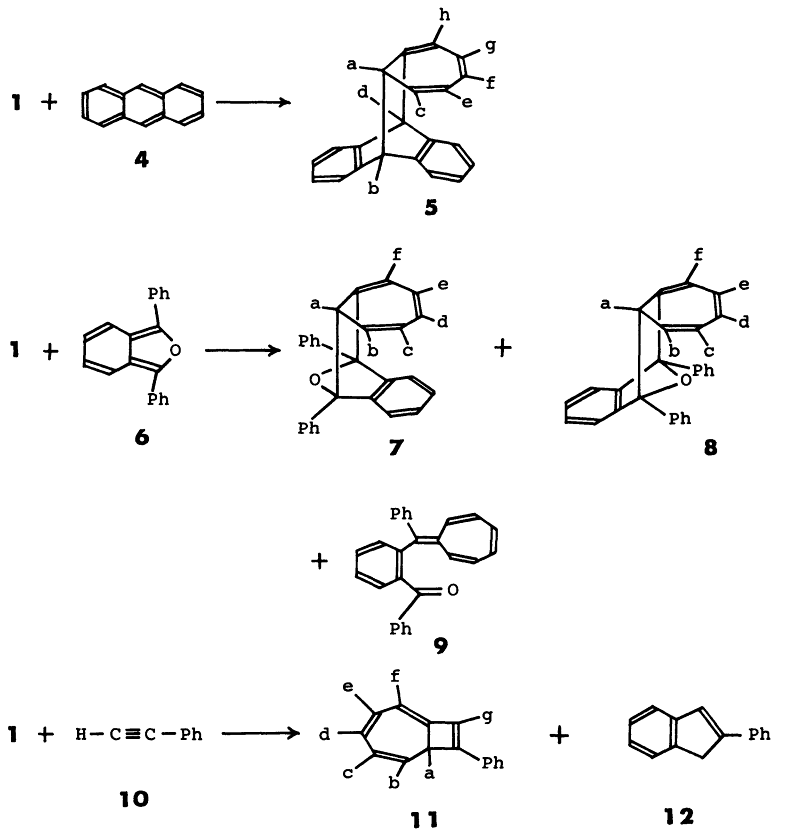

Fig. 2.

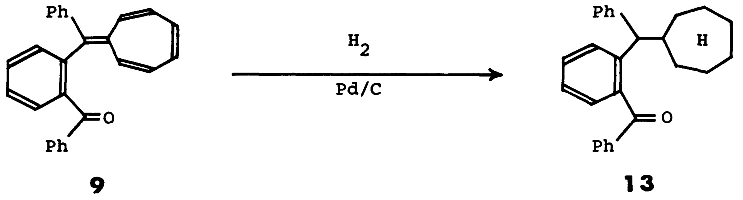

Fig. 3.

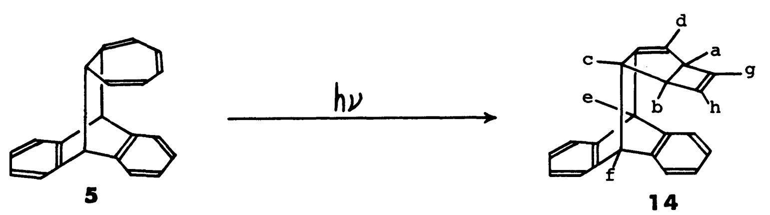

Fig. 4.

consistent with that of the bridge-head proton of the endo-adduct of **6** with cycloheptatriene (δ 3.88)[5d] and that of H_a of **5** (δ 2.46), respectively, indicating that each pair of protons is located in nearly the same chemical environment.

The structure of **9** was deduced mainly from its UV spectrum, which is characteristic of heptafulvene derivatives,[6] and its IR spectrum, which shows a carbonyl band in the same region as that of benzophenone. The absorbing of 4 molar equivalents of hydrogen by **9** to give a stable colorless oil **13** seems to support the structure of **9**.[6d]

The structure of the photoproduct **14** was deduced on the basis of the physical properties and confirmed by a comparison of the physical properties with those of the analogous compounds.[7]

Discussion

The mechanism for the formation of **9** from **7** and **8** initially involves the cleavage of the bond at 7-position of the cycloheptatriene moiety of **7** and **8** to give a tropylium cation (**15a**) or a tropylium radical intermediate (**15b**), which in turn affords **9** *via* an ether bond cleavage as shown in Fig. 5. The stability of the tropylium cation and/or the tropylium radical[8] and

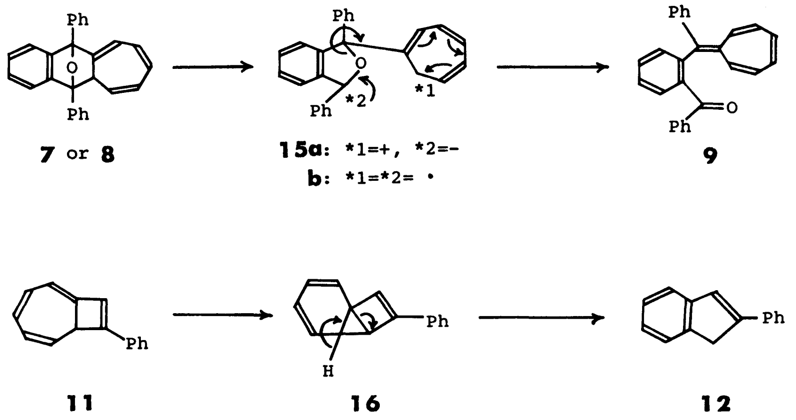

Fig. 5.

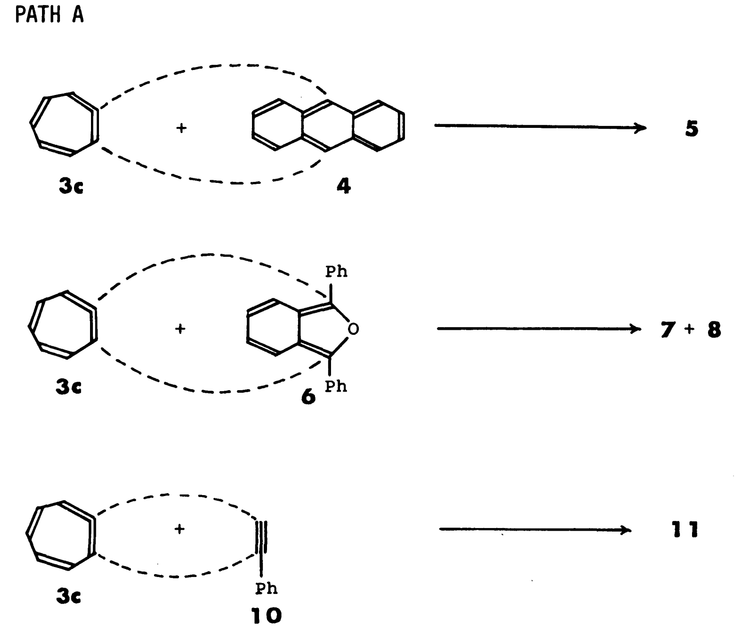

Fig. 6.

the formation of the stable benzophenone moiety can be regarded as the driving force for this reaction.

The isomerization mechanism of **11** to **12** may be explained as follows. The valence-bond isomerization of the cycloheptatriene moiety of **11** gives rise to the norcaradiene structure (**16**),9) which rearranges to **12** *via* a hydrogen shift. The analogous reaction mechanism has been proposed for the formation of indane derivatives in the thermal reactions of spiro[2.6]nona-4,6,8-triene derivatives.1b,7c,10) The photochemical formation of **14** proceeds *via* the well known 4 π-electrons photo-allowed disrotatory cyclization process.7,11)

Two possible mechanisms may be considered for the reaction of **1** with **4**, **6**, and **10**. Pathway A involves an allene intermediate **3c** followed by a [4+2] or [2+2] addition reaction of the allenic double bond of **3c** with the appropriate moieties of **4**, **6**, and **10** to give the corresponding adducts. Pathway B involves the carbene intermediate **3a**, which reacts with **4**, **6**, and **10** to afford the tropylium cation intermediates **17a**, **15a**, and **18a**, respectively, or the tropylium radical intermediates **17b**, **15b**, and **18b**, respectively. Subsequent cyclization reactions of these intermediates lead to the formation of the corresponding products.

A closer examination into pathway B reveals two facts which do not adequately explain the observed products. First, intermediate **3a** is a nucleophilic carbene; therefore, the addition of this carbene to **4**, **6**, and **10** is not favored since these compounds do not contain any electron-defficient double bonds. Second, the yield of the *endo*-adduct **7** is higher than that of the *exo*-adduct **8**. According to Dreiding model, there is no obvious difference between the steric repulsions in the formation of **7** and **8** from**15**. On this basis, **7** and **8** are expected to be formed in an equal yield from **15**. The fairly large difference between the yield of **7** and **8** would suggest that the reaction does not proceed *via* **15**. On the other hand, several advantages are envisioned regarding pathway A. Compounds **4** and **6** are known to react readily as 4π-components

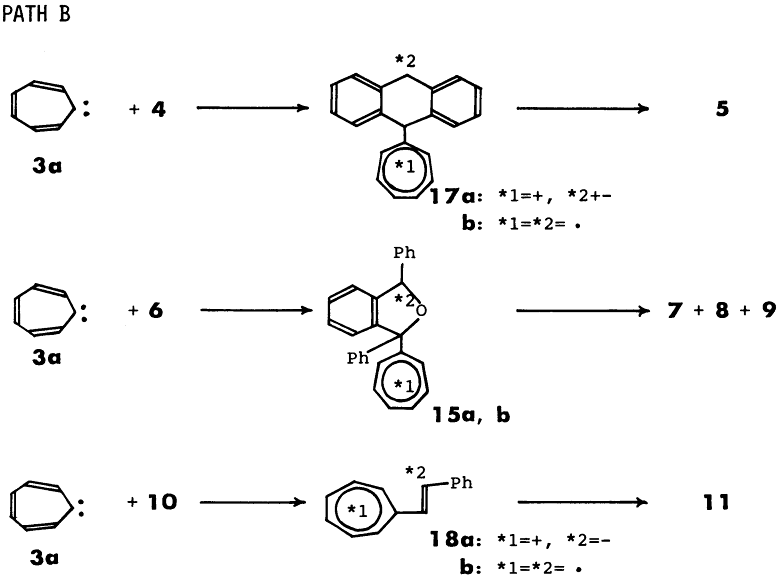

Fig. 7.

in [4+2]-type addition reactions.[12] Oda has reported that a cyclic conjugated allene derivative has been allowed to react with **6** to give *endo* and *exo* [4+2]-type adducts in a yield ratio of 5:1, without defining the stereochemistry of the adducts.[13] The major formation of the *endo*-adduct **7** can be explained as the result of the secondary orbital interaction in the transition state.[11]

As discussed above, it is difficult to decide whether the carbene intermediate **3a** or the allene intermediate **3c** is involved in the addition reactions, but a plausible pathway for the reaction would involve the allene intermediate **3c**. As for the reaction with **10**, pathway B seems to have still some possibility, because pathway A may involve a thermally forbidden [$\pi 2s+\pi 2s$] addition process.[14]

Experimental

The photoreactions were performed with a 400-W high-pressure mercury lamp, UVL-400P of Riko Kagaku Sangyo Ltd. under a nitrogen stream at room temperature. Thermal isomerizations were carried out in sealed ampoules. All melting points are uncorrected. UV and IR spectra were measured with the Hitachi 220A and DS-701G spectrometers, respectively. Mass spectra were measured with the Hitachi M-52 and JMS-DX300 spectrometers, and the NMR spectra were measured with a Hitachi R-20B or a Varian XL 200 spectrometer with tetramethylsilane as an internal standard. Wako Gel C-200 and activated alumina of Wako Pure Chemical Industries Ltd. were used for column chromatography. Wako Gel B5F was used for thin-layer chromatography.

Reaction of 1 with 4. A mixture of **1** (13.50 g, 46 mmol), **4** (25.00 g, 140 mmol) and anhydrous diglyme (120 ml) was heated at 120 °C for 15 min. After evolution of nitrogen gas had ceased (1l, 97%), the gray powder of **2** (7.70 g, 95%) was removed by filtration. The filtrate was extracted with benzene, washed with water, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to yield black crystals, which were recrystallized from benzene to give crystals of recovered **4** (21.29 g). The filtrate was chromatographed on silica gel to yield recovered **4** (0.85 g) by pet ether–benzene 9:1 and colorless crystals of **5** (2.57 g, 21%) by pet ether–benzene 8:2. The crystals of **5** were purified by recrystallization from benzene–ethanol. **5**: Mp 135—136 °C. Found: C, 93.80; H, 6.03%. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%. Mass m/z (rel intensity): 268 (M^+, 95), 191 (23), 178 (100). UV (EtOH): 276 nm (log ε, 3.53). IR (KBr): 3030, 1600, 1480 cm^{-1}. NMR ($CDCl_3$) δ=2.46 (m, H_a), 4.47 (d, H_b), 4.63 (dd, H_c), 4.78 (s, H_d), 5.86 (m, H_e), 6.20 (m, H_f, H_g, H_h), 7.0—7.5 (m, 8H, Ph). Coupling constants in Hz: J_{ab}=3, J_{ac}=5, J_{ce}=10, J_{ea}=2, J_{ef}=5.

Reaction of 1 with 6. A mixture of **1** (24.00 g, 80 mmol), **6** (43.00 g, 160 mmol) and anhydrous diglyme (200 ml) was heated at 120 °C for 15 min to evolve nitrogen gas (1.7 l, 96%). After separation of the gray powder of **2** (13.86 g, 96%) by filtration, the filtrate was treated, as usual, to yield a mixture of crystals and an oil. The crystals of recovered **6** (23.60 g) were separated by filtration and the filtrate was chromatographed on alumina to yield colorless crystals **7** (6.20 g) and mixed crystals of **7** and **8** (3.03 g) by pet ether–benzene 3:1 and a red oil **9** (1.15 g, 4%) by ether. The NMR spectrum of the mixed crystals showed that this mixture contained **7** and **8** in a ratio of 2:1. Thus, the yields of **7** and **8** were 8.22 g (28%) and 1.01 g (3%), respectively. Repeated recrystallization from benzene gave pure crystals of **7** and **8**. The red oil of **9** was further purified with thin-layer chromatography on silica gel using benzene as a developing solvent (R_f=0.60). 7: Mp 189—190 °C. Found: C, 90.23; H, 5.43%. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%. Mass m/z (rel intensity): 360 (M^+, 100), 255 (87), 105 (82). UV (EtOH): 278 nm (log ε, 3.44). IR (KBr): 3030, 1600, 1450 cm^{-1}. NMR ($CDCl_3$) δ=3.68 (m, H_a), 4.75 (dd, H_b), 5.85 (m, H_c), 6.13 (m, H_d), 6.20 (m, H_e, H_f), 7.0—7.8 (m, 14H, Ph). Coupling constants in Hz: J_{ab}=4, J_{ac}=2, J_{bc}=10, J_{cd}=5, J_{de}=11. **8**: Mp 177—178 °C. Found: C, 89.62; H, 5.59%. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%. Mass m/z (rel intensity): 360 (M^+, 45), 255 (100), 105 (55). UV (EtOH): 278 nm (log ε, 3.67). IR (KBr): 3030, 1600, 1450 cm^{-1}. NMR ($CDCl_3$) δ=2.60 (m, H_a), 5.15 (dd, H_b), 6.05 (m, H_c), 6.32 (m, H_d), 6.43 (m, H_e, H_f), 7.0—7.8 (m, 14H, Ph).

Coupling constants in Hz: $J_{ab}=4$, $J_{ac}=2$, $J_{bc}=10$, $J_{cd}=5$, $J_{de}=11$. **9**: Found: C, 90.22; H, 5.61%. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%. Mass m/z (rel intensity): 360 (M^+, 38), 209 (44), 152 (34), 105 (100). UV (EtOH): 248 nm (log ε, 4.32), 332 (3.93). IR (neat): 3030, 1670, 1600 cm^{-1}. NMR ($CDCl_3$) δ=5.3—6.5 (m, 6H), 7.0—7.4 (m, 14H, Ph).

Reaction of 1 with 10. A mixture of **1** (5.92 g, 20 mmol), **10** (10.20 g, 100 mmol), and anhydrous diglyme (50 ml) was heated at 120 °C for 15 min to evolve nitrogen gas (450 ml, 100%). After separation of the gray powder **2** (3.56 g, 100%), by filtration, the usual workup gave a black oil, which gave recovered **10** (7.69 g) by distillation under a reduced pressure (0.5 Torr[†], bath temperature 75 °C). The residue was chromatographed on silica gel to give a tarry material (680 mg) by pet ether, which was thin layer chromatographed on silica gel using pet ether as a developing solvent to give crystals of **12** (207 mg, 5%, R_f=0.45, mp 167—168 °C, lit,[4] 166—167 °C) and a colorless oil of **11** (320 mg, 8%, R_f=0.40). **11**: Found m/z 192.0967. Calcd for $C_{15}H_{12}$: 192.0964. Mass m/z (rel intensity): 192 (100), 179 (11), 165 (20), 115 (14). UV (EtOH): 270 nm (log ε, 4.23). IR (neat): 3050, 2960, 1660 cm^{-1}. NMR ($CDCl_3$) δ=4.71 (m, H_a), 5.21 (m, H_b), 5.75 (m, H_c), 5.8—6.7 (m, H_d, H_e, H_f), 6.37 (d, H_g), 7.1—7.5 (m, 5H, Ph). Coupling constants in Hz: $J_{ab}=4$, $J_{bc}=10$, $J_{ce}=5$, $J_{gf}=2$.

Hydrogenation of 9. A solution of **9** (150 mg, 0.42 mmol) in benzene (15 ml) was hydrogenated with palladium-charcoal (30 mg) to absorb hydrogen gas (38 ml, 17 mmol). After filtration, the solvent was removed on a rotary evaporator to yield a colorless oil, which was thin-layer chromatographed on silica gel using benzene as a developing solvent to yield a colorless oil of **13** (146 mg, 96%, R_f=0.70). **13**: Found: C, 87.97; H, 7.43%. Calcd for $C_{27}H_{28}O$: C, 88.00; H, 7.66%. Mass m/z (rel intensity): 368 (M^+, 100), 309 (57), 270 (44), 165 (24). UV (EtOH): 250 nm (log ε, 4.31). IR (neat): 3030, 2950, 1673, 1600 cm^{-1}. NMR ($CDCl_3$) δ=1.3—2.4 (two broad peaks, 14H), 7.0—7.4 (m, 14H, Ph).

Thermal Isomerization of 7. A solution of **7** (80 mg) in benzene (0.3 ml) was kept at 130 °C for 25 h in a sealed ampoule. Thin-layer chromatography of the reaction mixture on silica gel using benzene as a developing solvent gave mixed crystals of **7** and **8** (30 mg, R_f=0.85) and a red oil of **9** (34 mg, 42%, R_f=0.60). The NMR spectrum of the mixed crystals showed that the crystals contained **7** and **8** in a ratio of 5:1; thus,the yields of **7** and **8** were 25 mg (30%) and 5 mg (6%), respectively.

Thermal Isomerization of 8. A solution of **8** (80 mg) in benzene (0.3 ml) was kept at 130 °C for 25 h. Thin-layer chromatography of the reaction mixture under the same conditions as above gave mixed crystals of **7** and **8** (56 mg) and a red oil of **9** (16 mg, 20%). The NMR spectrum showed that the mixed crystals contained the recovered **7** (54 mg, 68%) and **8** (2 mg, 2%).

Thermal Isomerization of 11. A solution of **11** (40 mg) in benzene (5 ml) was kept at 120 °C for 1 h. After evaporation of the solvent, the reaction mixture was thin-layer chromatographed on silica gel using pet ether as a developing solvent to yield crystals of **12** (22 mg, 55%, R_f=0.45).

Photoreaction of 5. A solution of **5** (100 mg) in methanol (200 ml) was irradiated with a high-presssure mercury lamp for 2 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 yield a colorless oil of **14** (88 mg, 88%, R_f=0.80). **14**: Found: m/z 268.1227. Calcd for $C_{21}H_{16}$: m/z 268.1251. Mass m/z (rel intensity): 268 (14), 178 (100), 151 (7). UV (EtOH) 212 nm (sh, log ε, 4.45). IR (neat): 3030, 2980, 1460 cm^{-1}. NMR ($CDCl_3$) δ=2.76 (m, H_a), 3.10 (m, H_b), 4.19 (s, H_c), 4.35 (d, H_d), 5.54 (bs, H_e, H_f), 6.02 (d, H_g), 6.28 (d, H_h), 7.0—7.3 (m, 8H, Ph). Coupling constants in Hz: $J_{ab}=4$, $J_{ad}=3$, $J_{gh}=3$.

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[†] 1 Torr≈133.322 Pa.

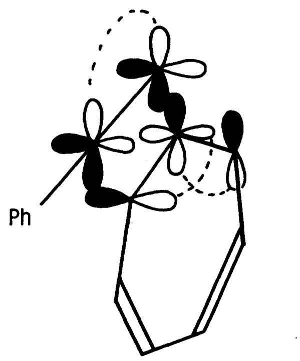

Fig. 8.

1975, 2587.

14) It is known that ketenes proceed [2+2]-type concerted addition reactions under thermal conditions, in which ketenes actually react as 4π components, forming thermally allowed [π4s+π2s] addition process.[15] The pathway A for the reaction of **3c** with **10** may be considered to be actually a thermally allowed [π4s+π2s] addition process, in which **3c** plays as a 4π component in the seemingly [2+2] type addition reaction as shown in Fig. 8.

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