Reactions of Cyclic C_7H_6-System: Reactions of a Tautomer of Cycloheptatetraene and Cycloheptatrienylidene with Tropone, Heptafulvene, and 1,3,5-Cycloheptatriene Derivatives

Katsuhiro SAITO,* Satoshi SUZUKI, Tetsuya WATANABE, and Kensuke TAKAHASHI
Department of Applied Chemistry, Nagaya Institute of Technology, Gokiso-cho, Showa-ku, Nagaya 466
(Received January 25, 1993)

Reactions of a cyclic C_7H_6-system, a tautomer of 1,2,4,6-cycloheptatetraene and 2,4,6-cycloheptatrienylidene, with tropone derivatives and 8,8-dicyanoheptafulvene afforded *exo*-[4π+2π] cycloadducts. Similar reactions with 1,3,5-cycloheptatriene derivatives gave *exo*-[6π+2π] cycloadducts. These reactions are considered to proceed through zwitter ionic intermediates containing tropylium ion moieties.

Much attention has been paid to the chemistry of strained multiple bonds incorporated in small- or medium-sized rings. Cycloaddition reactions of benzocyclopropene and benzocyclobutadiene have been studied for a long time in order to find [2π+4π] or [2σ+4π] reactions which to proceed.[1] Synthesis and [2π+4π] reactions of cumulenes constructing mediun-sized rings, such as 1,2-cyclohexadiene or 1,2,3-cyclohexatriene, are recent topics.[2] Some kinds of cyclic allenes are known to be interconvertible with the corresponding carbenes. Research on the mechanisms of this type of interconversion has progressed extensively.[2a,3]

Sodium salt of tropone tosylhydrazone (**1**) is known to generate a cyclic C_7H_6-system, which exists as a tautomer of a cyclic carbene (2,4,6-cycloheptatrienylidene (**2**) and a cyclic allene (1,2,4,6-cycloheptatetraene) (**3**) upon heating or irradiation. Molecular-orbital calculations have revealed that the energetically unfavorable cyclic carbene (**2**) exists as a transition state for an interconversion between the enantiomeric cyclic allenes (**3a** and **3b**).[4] Due to a contribution from a canonical structure (**2b**) the cyclic C_7H_6-system reacts as a nucleophilic singlet carbene with electron-defficient 2π electron components, such as maleonitrile or fumaronitrile, to give *cis*- or *trans*-spiro[2.6]nonatriene derivatives, stereospecifically.[5] On the other hand the cyclic C_7H_6-system reacts through the cyclic allene form (**3**) in [2π+4π] addition reactions with 4π electron components, such as anthracene or 2-pyrone derivatives.[6] Stereospecific *endo*-addition was reported in the reaction with 1,3-diphenylisobenzofuran thus suggesting that **3** reacted through a concerted [2π+4π] addition (Fig. 1).[7]

Cycloaddition reactions of seven-membered cyclic conjugated compounds such as tropone (**4**), heptafulvene (**5**), or 1,3,5-cycloheptatriene (**8**) derivatives have offered many stages for fruitfull discussions on experimental and theoretical research in line with the Woodward–Hoffmann rule.[8] Tropones (**4**) and heptafulvenes (**5**) are known to react with 2π electron components, such as acetylene or ethylene derivatives or benzyne, through [4π+2π] additions.[9] In exceptional cases, such as reactions with allene derivatives, **4** reacted as 8π electron components to give [8π+2π] cycloadducts via ionic mechanisms.[10]

The existence of a valence tautomerization is one of the reasons for so many papers being published concerning researches involving 1,3,5-cycloheptatriene derivatives (**8**). Thus, in reactions with 2π electron components **8** reacted through its norcaradiene form to give [4π+2π] cycloadducts via concerted mechanisms.[11] On the other hand, they acted as 6π electron units to give [6π+2π] cycloadducts in reactions with benzyne or cumulenes.[12]

In spite of many studies concerning the cycloaddition reactions of **4**, **5**, and **8** with olefins, there have been few studies concerning the reactions of these seven-membered cyclic conjugated compounds with cumulenes or carbene. We investigated the reactions of the cyclic C_7H_6-system (**2**, **3**) with 2-substituted tropones (**4**), 8,8-dicyanoheptafulvene (**5**), and 7-substituted 1,3,5-cycloheptatrienes (**8**) to form several types of cycloadducts. The results are discussed here.

Tropone tosylhydrazone sodium salt (**1**) was allowed to react with four molar amounts of tropone (**4a**) in anhydrous diglyme at 120 °C for 15 min. Chromatographic separation and purification of the reaction mixture gave an *exo*-[4π+2π] cycloadduct (**6a**) in 51% yield. Similar reactions of **1** with 2-substituted tropones, such as 2-phenyl- (**4b**), 2-methoxy- (**4c**), and 2-chlorotropone (**4d**), afforded the corresponding cycloadducts (**6b**—**6d**) in yields of 45, 23, and 12%, respectively. An analogous reaction proceeded in a heptafulvene derivative, though the yield was low. Thus, the reaction of **1** with 8,8-dicyanoheptafulvene (**5**) afforded the corresponding *exo*-[4π+2π] cycloadduct (**7**) in 2% yield (Fig. 2).

The reaction of **1** with 1,3,5-cycloheptatriene (**8a**) under the same conditions as mentioned above gave an *exo*-[6π+2π] cycloadduct (**9a**) in 19% yield. The analogous reactions of **1** with 7-substituted 1,3,5-cycloheptatrienes, such as 7-methyl- (**8b**), 7-ethyl- (**8c**), and 7-methoxy-1,3,5-cycloheptatriene (**8d**), afforded the corresponding cycloadducts (**9b**—**9d**) in 6, 5, and 14% yields, respectively. A similar reaction with 7-cyano-1,3,5-cycloheptatriene (**8e**) gave another type of *exo*-

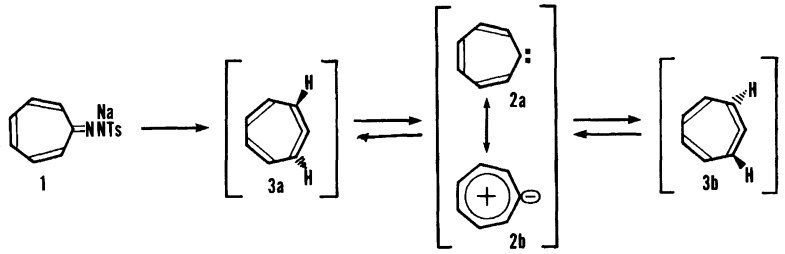

Fig. 1.

[6π+2π] cycloadduct (**9e**) in 7% yield (Fig. 3).

The structures of the [4π+2π] adducts, **6** and **7**, were deduced on the basis of their spectral, especially NMR, properties, and confirmed by their resemblance to those of the analogous compounds, such as [4π+2π] adducts of the 1-oxaazulene-2(1*H*)-one derivative (**10**) or **5** (**11**) (Fig. 4).[13] The absorption at ca. 1670 cm^{-1} in the IR spectra of 6 was reasonably attributed to the α,β-unsaturated carbonyl groups. The stereochemistries of these compounds were further supported by the existence of a 10% Nuclear–Overhouser effect between H_d and H_l in the NMR spectra of **6a**.

The structures of [6π+2π] adducts **9** were also deduced on the basis of their spectral properties and resemblance to those of the similar [6π+2π] adducts of **8a** (**12** or **13**).[6,7,12] The absence of coupling constants between H_b and H_d indicated that the dihedral angles between these protons are 80—100°.[14] According to Dreiding Models, the dihedral angles between these protons are ca. 20° in the *endo*-conformations and ca. 100° in the *exo*-confomations, thus showing the adducts (**9**) to be the *exo*-conformer. The dihedral angle measured with Dreiding Models between H_c and H_d (40°) and between H_c and H_e (20°) are very consistent with the observed coupling constant values of J_{cd} (5.2 Hz) and J_{ce} (6.7 Hz).[14] On the other hand, the dihedral angles between H_a and H_d (80°) and between H_a and H_e (100°) explain the absence of coupling constants between these protons in **9a**.

Upon heating, **9a** afforded a symmetric compound **14** (Fig. 5), whose structure was deduced on the basis of its NMR spectra; it showed five peaks, each of which corresponds to two protons (H_e, H_f, H_g, H_h, H_i) accompanied by four peaks corresponding to H_a, H_b, H_c, and H_d. This thermal rearrangement is well explained by a thermally allowed 1,5-hydrogen shift in **9a**, thus supporting the structure of **9a**.

Gomper et al. reported that the reactions of tropone with allene derivatives gave [8π+2π] cycloadducts or *endo*-[4π+2π] cycloadducts. The result of the present reaction of **1** with **4** or **5** to give *exo*-[4π+2π] cycloadducts (**6** or **7**) is obviously different from Gomper's

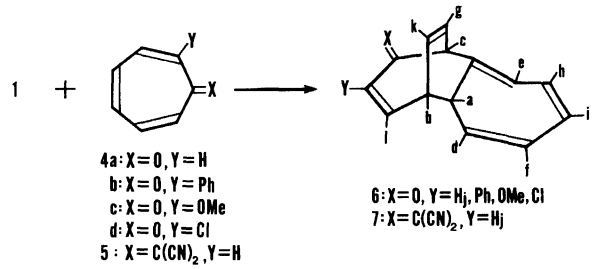

Fig. 2.

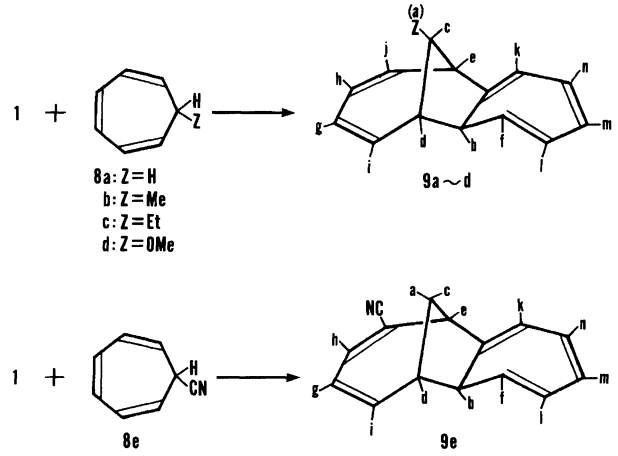

Fig. 3.

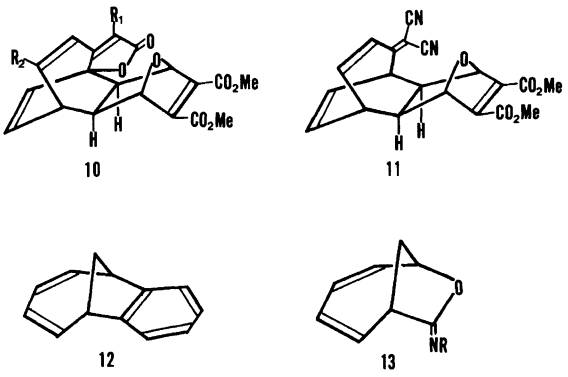

Fig. 4.

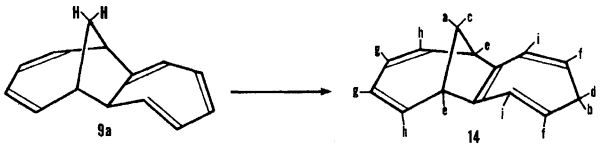

Fig. 5.

result.[10a] This discrepancy can be attributed to the difference between the stabilities of the intermediates in each reaction. Gomper proposed an ionic intermediate (**15**), which would have a stable tropylium ion moiety and an anion moiety stabilized by four electron-withdrawing groups (CO_2Et). Supposing that the present reactions proceeded with an analogous mechanism as those of Gomper, the intermediate in the present reaction should be **16** (Fig. 6). However, **16** must have an energetically unfavorable cycloheptatrienyl anion moiety. Thus, in the present reaction the ionic intermediate (**16**) can not be expected to be formed.

The present reactions with **4** or **5** are considered to proceed through the ionic intermediates **17**, whose anionic parts are stabilized by conjugations with the carbonyl (in the case of **4**) or dicyanomethylene groups (in the case of **5**). The ring closure needed to maintain most of the overlapping between the anionic and cationic parts in **17** (via A) can lead to the final products (**6**, **7**), rather than the *endo* adducts (**19**) via B (Fig. 7).[15]

The initial attact of the cyclic C_7H_6-system to **8** should occur from the site of the protons at the 7-position of **8** in order to avoid any steric repulsion caused by substituents at the 7-position. Considering the stability of the tropylium cation moieties, the present reactions with **8** are thought to proceed through ionic intermediates (**18**). The H–H steric repulsion (between the C-1 H of 2,4,6-cycloheptatrienyl and the C-2 H of 2,4,6-cycloheptatrienylium moieties) in *endo*-additions (via A) and the instability caused by stric repulsions in the *endo*-addition product (**20**) directed the reaction to proceed through *exo*-additions (via B) to give the final products (**9**) (Fig. 8). 1,3-Hydrogen shifts, which are known to proceed more easily in **8e** compared to the other 1,3,5-cycloheptatrienes (**8a**—**8d**) explain the formation of **9e**.[16]

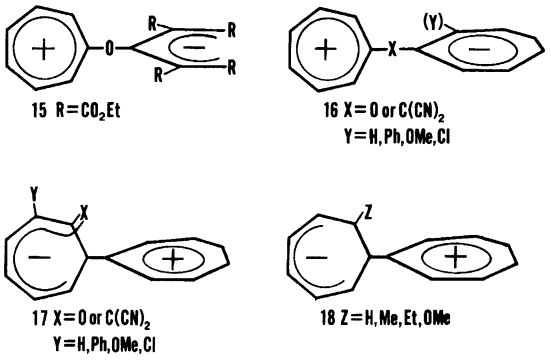

Fig. 6.

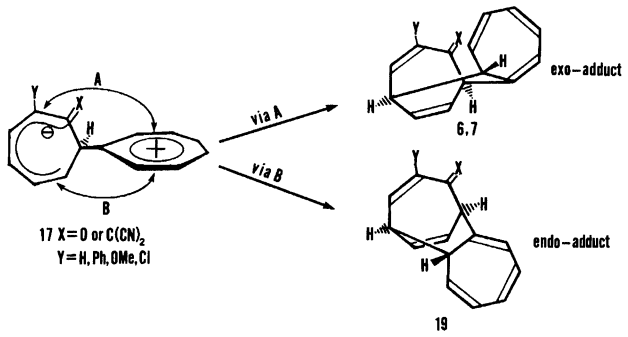

Fig. 7.

Experimental

NMR spectra were measured with a Varian XL-200 spectrometer with tetramethylsilane used as the internal standard. IR, UV, and MS spectra were measured with JASCO FT/IR-5300, Hitachi 220A, and Hitachi M-2000S spectrometers, respectively. Diglyme was distilled over calcium hydride and used immediately. Wakogel C-200 was used for column chromatography.

Only typical reactions are mentioned below.

Reaction of Tropone Tosylhydrazone Sodium Salt (1) with Troppone (4a). A mixture of **1** (5.92 g, 20 mmol) and **4a** (8.48 g, 80 mmol) in anhydrous diglyme (30 cm^3) was heated at 120 °C for 15 min. After filtration the mixture was poured into water, extracted with ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel to give an oil **6a** (2.0 g, 51%) with an eluent of hexane: ethyl acetate 9 : 1.

6a: HRMS: Found: m/z 196.0890. Calcd for $C_{14}H_{12}O$: M, 196.0888. MS m/z (rel intensity) 196 (M^+, 9), 195 (100), 166 (73), 152 (54), 140 (39). IR (neat) 3030, 2960, 1663, 1624 cm^{-1}. UV (EtOH) 239 (log ε, 3.72), 273 nm (sh, 3.39). ^1H NMR ($CDCl_3$) δ=2.63 (dd, H_a), 3.62 (ddd, H_b), 4.18 (dd, H_c), 4.90 (dd, H_d), 5.71 (d, H_j), 6.04—6.11 (m, 2H, H_e, H_f), 6.27 (dd, H_g), 6.40 (m, 2H, H_h, H_i), 6.56 (dd, H_k), 7.20 (dd, H_l). Coupling constants in Hz: J_{ab}=5.1, J_{ad}=4.2, J_{bk}=7.1, J_{bl}=7.9, J_{jl}=10.8. ^{13}C NMR ($CDCl_3$) δ=40.1, 44.1, 64.8, 122.8, 125.8, 126.6, 128.3, 129.0, 129.6, 130.0, 136.4, 153.4, 194.4.

6b: HRMS: Found: m/z 272.1203. Calcd for $C_{20}H_{16}O$: M, 272.1201. MS m/z (rel intensity) 272 (M^+, 22), 271 (100), 242 (36), 227 (29), 182 (53). IR (neat) 3020, 2950, 1670, 1630 cm^{-1}. UV (EtOH) 272 nm (log ε, 3.74). ^1H NMR ($CDCl_3$) δ=2.66 (dd, H_a), 3.72 (ddd, H_b), 4.35 (d, H_c), 4.98 (dd, H_d), 6.04—6.20 (m, 2H, H_e, H_f), 6.36 (dd, H_g), 6.42 (m, 2H, H_h, H_i), 6.60 (dd, H_k), 7.18—7.40 (m, 6H, H_e, Ph). Coupling constants in Hz: J_{ab}=4.6, J_{ad}=4.6, J_{bk}=6.4, J_{bl}=7.9, J_{cg}=6.6, J_{df}=9.6, J_{eh}=3.6, J_{fi}=3.6, J_{gk}=7.6. ^{13}C NMR ($CDCl_3$) δ=40.3, 44.1, 65.3, 122.9, 125.5, 126.8, 127.5, 127.8, 128.9, 129.4, 129.7, 130.1, 136.1, 136.3, 137.8, 138.5, 150.8, 193.1.

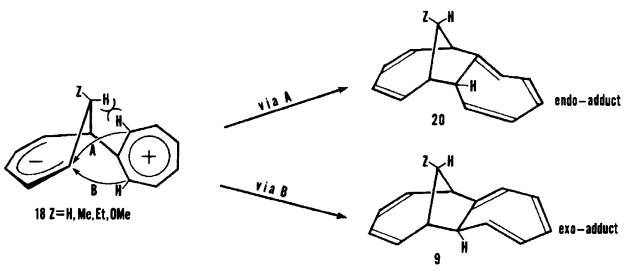

Fig. 8.

6c: HRMS: Found: m/z 226.0979. Calcd for $C_{15}H_{14}O_2$: 226.0993. MS m/z (rel intensity) 226 (M^+, 10), 225 (80), 182 (100), 154 (83), 127 (80). IR (neat) 3030, 2960, 1680, 1638, 1619 cm^{-1}. UV (EtOH) 269 nm (log ε, 3.58). ^1H NMR ($CDCl_3$) δ=2.66 (dd, H_a), 3.70 (m, H_b), 3.57 (s, 3H, Me), 4.33 (d, H_c), 4.93 (dd, H_d), 6.07—6.18 (m, 2H, H_e, H_f), 6.22—6.40 (m, 4H, H_g, H_h, H_i, H_l), 6.67 (dd, H_k). Coupling constants in Hz: J_{ab}=5.0, J_{ad}=4.2, J_{bl}=7.9, J_{bk}=7.2, J_{cg}=6.8, J_{df}=9.4, J_{gk}=7.2. ^{13}C NMR ($CDCl_3$) δ=37.4, 43.3, 54.8, 63.5, 119.1, 123.2, 126.5, 126.6, 128.3, 129.8, 129.9, 136.0, 137.8, 149.2, 190.4.

6d: HRMS: Found: m/z 230.0511. Calcd for $C_{14}H_{11}OCl$: M, 230.0497. MS m/z (rel intensity) 230 (M^+, 35), 195 (45), 167 (100), 165 (71), 152 (46). IR (neat) 3023, 2924, 1682, 1632, 1599 cm^{-1}. UV (MeCN) 213 (log ε, 4.01) and 238 nm (sh, 3.77). ^1H NMR ($CDCl_3$) δ=2.67 (m, H_a), 3.77 (m, H_b), 4.48 (dd, H_c), 4.94 (dd, H_d), 6.14 (m, H_f), 6.20 (m, H_e), 6.38 (ddd, H_g), 6.44—6.49 (m, 2H, H_h, H_i), 6.66 (ddd, H_k), 7.54 (d, H_l). Coupling constants in Hz: J_{ab}=5.2, J_{ad}=4.5, J_{bl}=9.4, J_{bk}=7.2, J_{bg}=1.2, J_{cg}=7.0, J_{ck}=1.1, J_{df}=9.9, J_{fi}=2.1, J_{eh}=2.4, J_{gk}=8.2. ^{13}C NMR ($CDCl_3$) δ=40.2, 43.5, 63.2, 123.6, 125.3, 127.0, 129.1, 129.9, 130.0, 131.2, 134.5, 136.2, 149.5, 187.5.

7: HRMS: Found: m/z 244.1006. Calcd for $C_{17}H_{12}N_2$: M, 244.1001. MS m/z (rel intensity) 244 (M^+, 5), 242 (100), 227 (24), 215 (53), 177 (50). IR (neat) 3040, 2970, 2230, 1607, 1540 cm^{-1}. UV (EtOH) 293 nm (log ε, 4.06). ^1H NMR ($CDCl_3$) δ=2.67 (dd, H_a), 3.70, (m, H_b), 4.65, (d, H_c), 4.91 (dd, H_d), 6.11 (m, 2H, H_e, H_f), 6.27 (dd, H_g), 6.28 (dd, H_h), 6.46 (dd, H_i), 6.54 (dd, H_j), 6.64 (dd, H_k), 7.09 (dd, H_l). Coupling constants in Hz: J_{ab}=4.8, J_{ad}=4.8, J_{bj}=2.0, J_{bk}=7.2, J_{bl}=7.5, J_{cg}=6.3, J_{df}=9.5, J_{eh}=5.0, J_{fi}=5.0, J_{gk}=7.9, J_{hi}=6.5, J_{jl}=10.5. ^{13}C NMR ($CDCl_3$) δ=40.4, 44.9, 52.3, 77.3, 111.9, 113.0, 123.5, 125.3, 126.1, 127.0, 128.7, 129.7, 130.5, 136.9, 137.6, 152.1, 169.1.

Reaction of 1 with 1,3,5-Cycloheptatriene (8a). A mixture of **1** (5.93 g, 20 mmol) and **8a** (7.36 g, 80 mmol) in anhydrous diglyme (30 cm^3) was heated at 120 °C for 15 min. After filtration the mixture was poured into water, extracted with ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel to give an oil **9a** (685 mg, 19%) with an eluent of hexane: ethyl acetate 19 : 1.

9a: HRMS: Found: m/z 182.1087. Calcd for $C_{14}H_{14}$: M, 182.1094. MS m/z (rel intensity) 182 (M^+, 43), 178 (91), 165 (100), 128 (65). IR (neat) 3015, 2957, 2924, 2856, 2361 cm^{-1}. UV (EtOH) 205 (log ε, 4.16), 256 nm (3.71). ^1H NMR ($CDCl_3$) δ=2.10 (d, H_a), 2.40—2.53 (M^+, 2H, H_b, H_c), 2.86 (dd, H_d), 3.54 (dd, H_e), 5.01 (dd, H_f), 5.64—5.76 (m, 2H, H_g, H_h), 6.01—6.12 (m, 4H, H_i, H_j, H_k, H_l), 6.40—6.64 (m, 2H, H_m, H_n). Coupling constants in Hz: J_{ac}=12.2, J_{bf}=4.6, J_{cd}=5.2, J_{ce}=6.7, J_{di}=7.4, J_{ej}=8.0, J_{fl}=8.9, J_{kn}=5.7, J_{lm}=5.7, J_{mn}=11.4. ^{13}C NMR ($CDCl_3$) δ=32.1, 44.0, 45.7, 56.5, 116.2, 123.0, 123.7, 123.9, 124.2, 127.8, 131.3, 135.1, 137.0, 149.7.

9b: HRMS: Found: m/z 196.1258. Calcd for $C_{15}H_{16}$: M, 196.1252. MS m/z (rel intensity) 196 (M^+, 55), 181 (100), 167 (47), 165 (68), 153 (49), 152 (60). IR (neat) 3015, 2924, 2872, 1698, 1601 cm^{-1}. UV (EtOH) 204 (log ε, 4.24) and 257 nm (3.90). ^1H NMR ($CDCl_3$) δ=1.07 (d, 3H, Me, J=6.3 Hz), 2.42 (m, H_b), 2.64—2.70 (m, 2H, H_c, H_d), 3.36 (m, H_e), 5.04 (dd, H_f), 5.70—5.98 (m, 4H, H_g, H_h, H_i, H_j), 6.01—6.10 (m, 2H, H_k, H_l), 6.38—6.61 (m, 2H, H_m, H_n). Coupling constants in Hz: J_{bf}=4.7, J_{fl}=9.3, J_{kn}=5.2, J_{lm}=5.2, J_{mn}=11.4. ^{13}C NMR ($CDCl_3$) δ=12.8, 34.1, 48.8, 50.7, 57.4, 116.6, 123.8, 124.3, 125.2, 126.0, 127.9, 131.2, 131.8, 134.3, 151.4.

9c: HRMS: Found: m/z 210.1426. Calcd for $C_{16}H_{18}$: M, 210.1408. MS m/z (rel intensity) 210 (M^+, 83), 181 (100), 167 (63), 165 (61), 128 (63). IR (neat) 3015, 2959, 2919, 2866, 1599, 1458, 1377 cm^{-1}. UV (EtOH) 203 (log ε, 4.28) and 256 nm (3.88). ^1H NMR ($CDCl_3$) δ=0.93 (t, 3H, CH_3 of Et, J=6.7 Hz), 1.50 (dq, 2H, CH_2 of Et, J=6.7 and 6.7 Hz), 2.37—2.51 (m, 2H, H_b, H_c), 2.74 (dd, H_d), 3.44 (dd, H_e), 5.03 (dd, H_f), 5.69—5.98 (m, 4H, H_g, H_h, H_i, H_j), 6.01—6.10 (m, 2H, H_k, H_l), 6.38—6.61 (m, 2H, H_m, H_n). Coupling constants in Hz: J_{bf}=4.2, J_{cd}=4.2, J_{ce}=5.2, J_{di}=6.2, J_{ej}=7.4, J_{fl}=9.3, J_{kn}=5.7, J_{lm}=5.7, J_{mn}=11.0. ^{13}C NMR ($CDCl_3$) δ=13.3, 20.7, 42.1, 46.9, 48.9, 56.8, 116.6, 123.7, 124.2, 125.2, 125.9, 127.8, 131.1, 131.7, 134.3, 151.0.

9d: HRMS: Found: m/z 212.1190. Calcd for $C_{15}H_{16}O$: M, 212.1199. MS m/z (rel intensity) 212 (M^+, 99), 167 (100), 141 (54), 128 (59). IR (neat) 3019, 2924, 2824, 1701, 1130 cm^{-1}. UV (EtOH) 203 (log ε, 4.25) and 256 nm (3.78). ^1H NMR ($CDCl_3$) δ=2.41 (d, H_b), 3.04 (m, H_d), 3.43 (s, 3H, Me), 3.73 (m, H_e), 4.34 (dd, H_c), 5.09 (dd, H_f), 5.89 (m, 4H, H_g, H_h, H_i, H_j), 6.02—6.09 (m, 2H, H_k, H_l), 6.42—6.63 (m, 2H, H_m, H_n). Coupling constants in Hz: J_{bf}=4.6, J_{cd}=5.0, J_{ce}=6.1, J_{di}=5.2, J_{ej}=7.3, J_{fl}=9.2, J_{kn}=5.7, J_{lm}=5.7, J_{mn}=11.4. ^{13}C NMR ($CDCl_3$) δ=46.1, 47.9, 54.4, 57.9, 77.2, 118.3, 123.6, 124.5, 125.7, 126.4, 128.5, 129.2, 131.2, 131.8, 145.1.

9e: HRMS: Found: m/z 207.1052. Calcd for $C_{15}H_{13}N$: M, 207.1047. MS m/z (rel intensity) 207 (M^+, 100), 192 (57), 179 (54), 165 (64), 153 (55), 129 (69). IR (neat) 3017, 2928, 2861, 2363, 2203, 1582 cm^{-1}. UV (MeCN) 208 (log ε, 4.08) and 270 nm (3.91). ^1H NMR ($CDCl_3$) δ=2.14 (d, H_a), 2.46 (bs, H_b), 2.57 (m, H_c), 2.98 (dd, H_d), 3.70 (d, H_e), 5.01 (dd, H_f), 5.78 (dd, H_g), 6.08 (m, H_l), 6.27 (d, H_k), 6.40—6.78 (m, 4H, H_h, H_i, H_m, H_n). Coupling constants in Hz: J_{ac}=12.7, J_{bf}=4.7, J_{cd}=4.7, J_{ce}=6.8, J_{di}=8.0, J_{fl}=9.3, J_{gh}=7.8, J_{gi}=11.6, J_{kn}=5.1, J_{lm}=5.3. ^{13}C NMR ($CDCl_3$) δ=31.6, 45.6, 46.3, 56.8, 117.7, 122.1, 123.0, 124.7, 129.0, 130.9, 137.5, 145.3.

Thermal Rearrangement of 9a. A solution of **9a** (66 mg, 0.36 mmol) in diglyme (3 cm^3) was refluxed for 1 d. After filtration the mixture was poured into water, extracted with ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent gave a mixture of **14** (76%, 50 mg); the recovery (**9a**) (21%, 14 mg) whose ratios was determined by NMR.

14: HRMS: Found: m/z 182.1094. Calcd for $C_{14}H_{14}$: M, 182.1094. MS m/z (rel intensity) 182 (M^+, 82), 181 (41), 167 (93), 165 (100), 141 (56). IR (neat) 2963, 1262, 1093, 1020 cm^{-1}. UV (EtOH) 203 (log ε, 3.70) and 254 nm (3.32). ^1H NMR ($CDCl_3$) δ=1.71 (d, H_a), 2.04 (m, H_b), 2.32—2.50 (m, 2H, H_c, H_d), 3.44 (dd, 2H, H_e), 5.31 (m, 2H, H_f), 5.80 (dd, 2H, H_g), 6.19—6.30 (m, 4H, H_h, H_i). Coupling constants in Hz: J_{ac}=11.6, J_{bd}=13.0, J_{bf}=6.4, J_{ce}=7.1, J_{df}=6.9, J_{eh}=7.1, J_{fi}=9.1, J_{gh}=8.8, J_{gh}=3.2. ^{13}C NMR ($CDCl_3$) δ=26.5, 29.2, 46.2, 118.1, 123.2, 123.4, 138.8, 138.9.

References

1) B. Halton and M. C. Banwell, "Cyclopropenes," in "The Chemistry of Functional Groups," Wiley, Chichester (1987), pp. 1223—1340; K. Saito, H. Ishihara, and K. Kagabu, *Bull. Chem. Soc. Jpn.*, **60**, 4141 (1987); S. Kagabu, K. Saito, H. Watanabe, K. Takahashi, and K. Wada, *Bull. Chem. Soc. Jpn.*, **64**, 106 (1991).

2) a) R. P. Johnson, *Chem. Rev.*, **89**, 1111 (1989); b) C. W. Shakespere and R. P. Johnson, *J. Am. Chem. Soc.*, **112**, 578 (1990).

3) W. M. Jones and D. L. Krause, *J. Am. Chem. Soc.*, **93**, 551 (1971); H. G. Zoch, G. Szeimies, R. Romer, G. Germain, and J. P. Declercq, *Chem. Ber.*, **116**, 2285 (1983); J. P. Price and R. P. Johnson, *Tetrahedron Lett.*, **27**, 4679 (1986).

4) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, **99**, 6179 (1977); E. E. Waali, *J. Am. Chem. Soc.*, **103**, 3604 (1981); C. L. Janssen and H. F. Schaefer, *J. Am. Chem. Soc.*, **109**, 5030 (1987).

5) W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **89**, 3069 (1967); T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, **1968**, 565; W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **91**, 6391 (1969); L. W. Christensen, E. E. Waali, and W. M. Jones, *J. Am. Chem. Soc.*, **94**, 2118 (1972).

6) J. W. Harris and W. M. Jones, *J. Am. Chem. Soc.*, **104**, 7329 (1982); K. Saito and H. Ishihara, *Bull. Chem. Soc. Jpn.*, **58**, 2664 (1985); K. Saito and H. Ishihara, *Bull. Chem. Soc. Jpn.*, **59**, 1095 (1986); K. Saito and H. Ishihara, *Bull. Chem. Soc. Jpn.*, **60**, 4447 (1987); K. Saito, T. Watanabe, and K. Takahashi, *Chem. Lett.*, **1989**, 2099.

7) K. Saito, Y. Omura, and T. Mukai, *Chem. Lett.*, **1980**, 349; K. Saito, Y. Omura, and T. Mukai, *Bull. Chem. Soc. Jpn.*, **58**, 1663 (1985).

8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

9) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960); M. Oda and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **43**, 1920 (1970).

10) a) R. Gomer and U. Wolf, *Justus Liebigs Ann. Chem.*, **1979**, 1388; b) R. P. Gandhi and M. P. S. Ishar, *Chem. Lett.*, **1989**, 101.

11) W. Adam, M. Balci, and B. Pietrzak, *J. Am. Chem. Soc.*, **101**, 6285 (1979); T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Jpn.*, **42**, 2033 (1969); K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

12) E. J. Moriconi, C. F. Hummel, and J. F. Kelly, *Tetrahedron Lett.*, **1969**, 5325; S. Ito, S. Narita, and K. Endo, *Bull. Chem. Soc. Jpn.*, **46**, 3517 (1973); E. J. Moriconi and C. F. Hummel, *J. Org. Chem.*, **41**, 3583 (1976).

13) R. Tian, S. Sugiyama, A. Mori, H. Takeshita, M. Higashi, and Y. Yamaguchi, *Chem. Lett.*, **1988**, 941.

14) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

15) An electric attraction force can exist between the anionic part and the tropylium ion part in **17**. The main charge of the anion part is considered to exist close to the carbonyl or dicyanomethylene groups. Thus, the electric attraction force A (between the main anionic part and the tropylium part) should be larger than B.

16) K. Takahashi, H. Yamamoto, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, **43**, 200 (1970).