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[4+2]-Type Cycloadditions of Tropone and Heptafulvene Derivatives with a Tautomeric Mixture of Cycloheptatrienylidene and Cycloheptatetraene

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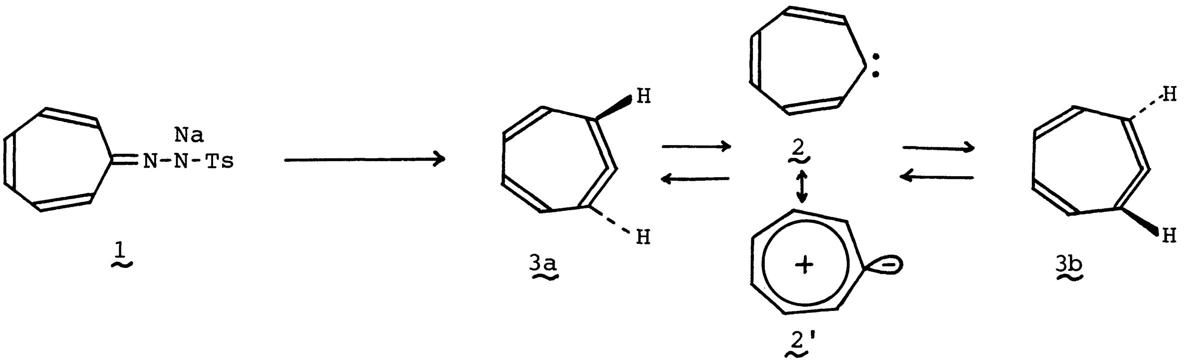
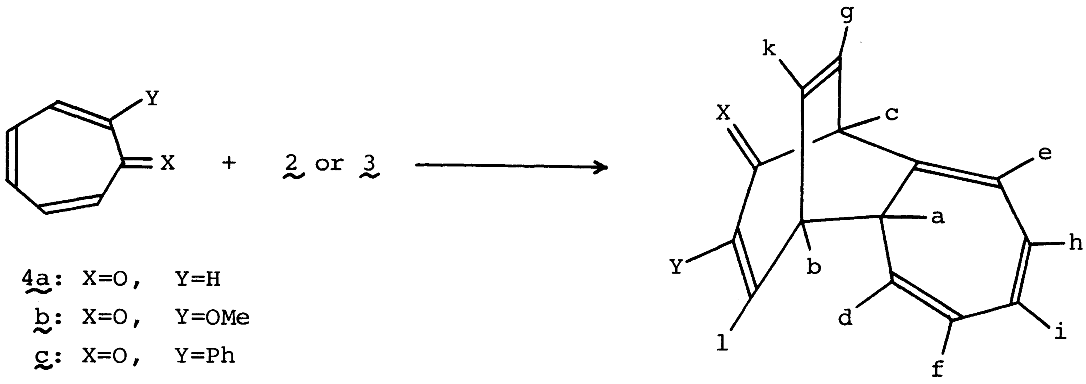
Reactions of tropone derivatives and 8,8-dicyanoheptafulvene with a tautomeric mixture of cycloheptatrienylidene and 1,2,4,6-cycloheptatetraene afforded [4+2]-type cycloadducts.

While many reports have been published which said that tropone and heptafulvene derivatives gave [8+2]- and/or [4+2]-type cycloadducts in thermal reactions with various kinds of olefins,[1)] the reactions with allenes or carbenes have scarcely been investigated. It is known that the reactions of tropones with allenes afforded solely [8+2]-type cycloadducts.[2)] However, a recent report has disclosed that some kinds of allenes gave [4+2]-type cycloadducts in the reactions with tropone.[3)] On the other hand, we are unaware of any reports concerning the reactions of heptafulvenes with allenes. The reactions of tropone and heptafulvene derivatives with carbenes have also been scarcely reported.

Tropone tosylhydrazone sodium salt (**1**) is known to generate a seven-membered cyclic carbene, cycloheptatrienylidene (**2**) by thermolysis or photolysis.[4)] Recent studies on **2** have shown that **2** tautomerized to a seven-membered cyclic allene, 1,2,4,6-cycloheptatetraene (**3**), and also **3** tautomerized to **2**. Thus, **2** and **3** exist as a tautomeric mixture and **2** is the transition state for the interconversion of the enantiometric cyclic allene (**3a** and **3b**).[5)] Experimental studies have revealed that **2** behaved as a singlet nucleophilic carbene toward electron-deficient olefins to give spiro[2.6]nonatrienes, while **3** reacted as a dienophile in [4+2]-type cycloadditions toward cyclic dienes to give bicyclo-[5.4.0]undecatetraenes.[4,6)]



In order to investigate the reactivities of tropone and heptafulvene derivatives with this tautomeric mixture of **2** and **3**, we studied the reactions of tropones (**4**) and 8,8-dicyanoheptafulvene (**6**) with **1** and found a novel reaction giving exo-[4+2]-type cycloadducts (**5** and **7**). Here the results are discussed.



4a: X=O, Y=H
b: X=O, Y=OMe
c: X=O, Y=Ph
6: X=C(CN)$_2$, Y=H

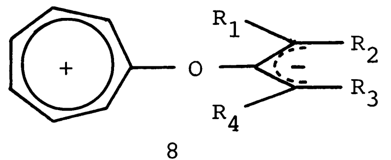
5a: X=O, Y=H$_j$
b: X=O, Y=OMe
c: X=O, Y=Ph
7: X=C(CN)$_2$, Y=H$_j$

Four molar equivalents of tropone (**4a**) was reacted with **1** in anhydrous diglyme at 120 °C to give the adduct **5a** in 51.1% yield. The similar reactions using 2-methoxytropone (**4b**), 2-phenyltropone (**4c**), and 8,8-dicyanoheptafulvene (**6**) afforded the corresponding adducts **5b**, **5c**, and **7** in 22.5, 45.0, and 2.3% yields, respectively.

The structures of the adducts were deduced on the basis of their spectra,[7] especially NMR spectra, and by their resemblance to those of the analogous compounds,[6,8] especially to those of the exo-[4+2]-type adduct of **6** reported by Takeshita et al.[8] The stereochemistries of the adducts were further confirmed by the existence of a 10% Nuclear-Overhauser effect in the NMR spectra between H$_d$ and H$_l$.

According to Kende et al., tropone affords a [4+2]-type cycloadduct in the reaction with benzyne.[9] On the other hand, Kitahara et al. have documented that 8-cyanoheptafulvene reacted with benzyne to afford a [8+2]-type cycloadduct.[10] Thus, tropone and 8-cyanoheptafulvene behave in the different manner toward benzyne. In the present case, tropone and 8,8-dicyanoheptafulvene behave in the same manner toward a tautomeric mixture of **2** and **3**.

The structural analysis shows that the reactions proceeded formally in an exo-[4+2]-type cycloadditions of the allene **3**. This result is different from the results reported in the preceding literatures, which say that the reactions of **4a** with allenes gave [8+2]-type cycloadducts[2] or endo-[4+2]-type cycloadducts.[3] This difference is considered to be partially attributable to the existence of the ionic intermediate of the type **8**, which was proposed by Gomper et al.[2,3] as an intermediate in the reaction of **4a** with allenes to direct the reaction to [8+2]-type addition. Supposing that **2** or **3** attacks the carbonyl or dicyanomethylene groups of **4** or **5** in the same manner as the case of Gomper et al., an ionic intermediate (**9**) should be formed. The intermediate **8** can be stabilized by the electron-attracting substituents (R_{1-4}=CO_2Et). However, **9** has no efficient substituent to stabilize the anionic part. Moreover, **9** must have a cycloheptatrienyl anion moiety which is energetically unfavorable. Thus in the present case, the ionic intermediate (**9**), which leads to [8+2]-type cycloadducts, can not be expected to be formed.



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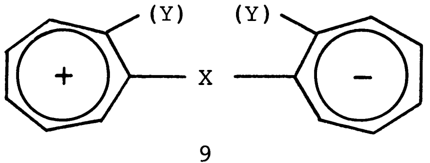

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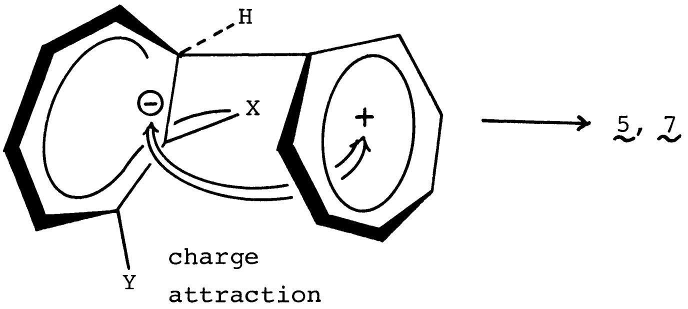

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The present reaction can be considered to proceed through an ionic intermediate (**10**), which is derived from a nucleophilic attack of **2** or **3** to the 7-positions of **4** or **6**.4,6) The anion moiety of **10** is stabilized by conjugation with the carbonyl or dicyanomethylene groups and the tropylium cation moiety enjoys an aromatic stabilization. An electric attraction between the anionic and cationic parts sets the each part as shown in the figure; The tropylium cation part is located close to the carbonyl or dicyanomethylene groups which are negatively charged more than the other part of the anionic part of **10**. The ring closure to maintain the most overlaping between the anionic and the cationic parts in **10** can lead to the final adducts.3,11)

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7) The spectral properties of the adducts are as follows:

5a: Mass m/z (rel intensity) 196 (M^+, 9), 195 (100); IR (oil) 3030, 2960, 1663, 1624 cm^{-1}; UV (EtOH) 239 nm (sh., log ε, 3.72), 273 nm (sh., log ε, 3.39); ^{1}H NMR ($CDCl_3$) δ 2.63 (dd, H_a), 3.62 (dd, H_b), 4.18 (d, H_c), 4.90 (dd, H_d), 5.71 (d, H_j), 6.04-6.11 (m, H_e, H_f), 6.27 (dd, H_g), 6.40 (m, 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_{ce}=2.4, J_{cg}=5.8, J_{df}=9.3, J_{eh}=3.6, J_{fi}=3.6, J_{gk}=8.0, J_{jl}=10.8.

5b: Mass m/z (rel intensity) 226 (M^+, 10), 225 (80), 182 (100); IR (oil) 3030, 2960, 1680, 1638 cm^{-1}; UV (EtOH) 269 nm (log ε, 3.58); ^{1}H NMR ($CDCl_3$) δ 2.66 (dd, H_a), 3.70 (m, H_b), 3.57 (s, 3H), 4.33 (d, H_c), 4.93 (dd, H_d), 6.07-6.18 (m, H_e, H_f), 6.22-6.40 (m, 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.

5c: Mass m/z (rel intensity) 272 (M^+, 22), 271 (100), 242 (36), 182 (53); IR (oil) 3020, 2950, 1670, 1630 cm^{-1}; UV (EtOH) 272 nm (log ε, 374); ^{1}H NMR ($CDCl_3$) δ 2.66 (dd, H_a), 372 (dd, H_b), 4.35 (d, H_c), 4.98 (dd, H_d), 6.04-6.20 (m, H_e, H_f), 6.36 (dd, H_g), 6.42 (m, H_h, H_i), 6.60 (dd, H_k), 7.18-7.40 (m, 6H, H_l, 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.

7: Mass m/z (rel intensity) 244 (M^+, 5), 242 (100), 215 (53), 177 (50); IR (oil) 3040, 2970, 2230, 1607 cm^{-1}; UV (EtOH) 293 nm (log ε, 4.06); ^{1}H NMR ($CDCl_3$) δ 2.67 (dd, H_a), 3.70 (dd, H_b), 4.65 (d, H_c), 4.91 (dd, H_d), 6.11 (m, H_e, H_f), 6.27 (dd, H_g), 6.28 (dd, H_h), 6.466 (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_{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.

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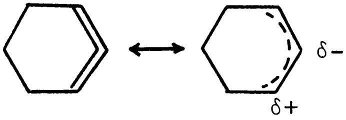
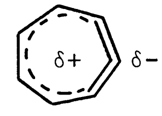
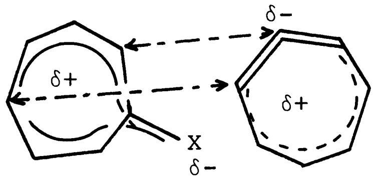
11) It is hard to rule out the following mechanism; A small-membered cyclic allene (**11**) is known to have a nucleophilicity probably because of a contribution of an ionic structure (**11'**).[12] The carbene **2** can enjoy a contribution of a 6 π-electrons aromatic structure (**2'**). These facts may allow to consider **3** to contain a contribution of an ionic form **3'**. A concerted [4+2]-type addtion of **3'** with **4** or **6** to maintain the most overlapping between the cationic and the anionic parts as shown in **12** can give the final adducts.



11 **11'**



3'



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