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(4+2) TYPE CYCLOADDITIONS OF CYCLOHEPTATRIENYLIDENE TO ANTHRACENE AND 1,3-DIPHENYLISOBENZOFURAN

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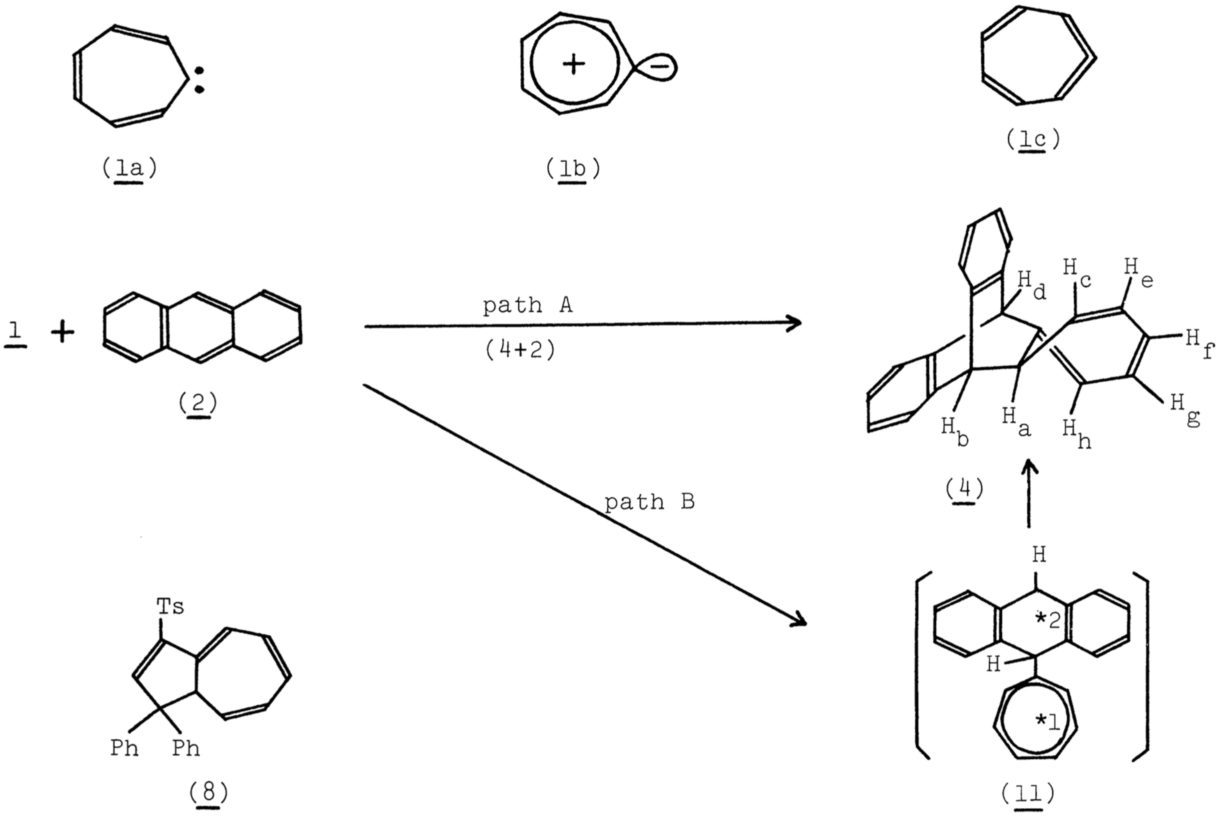
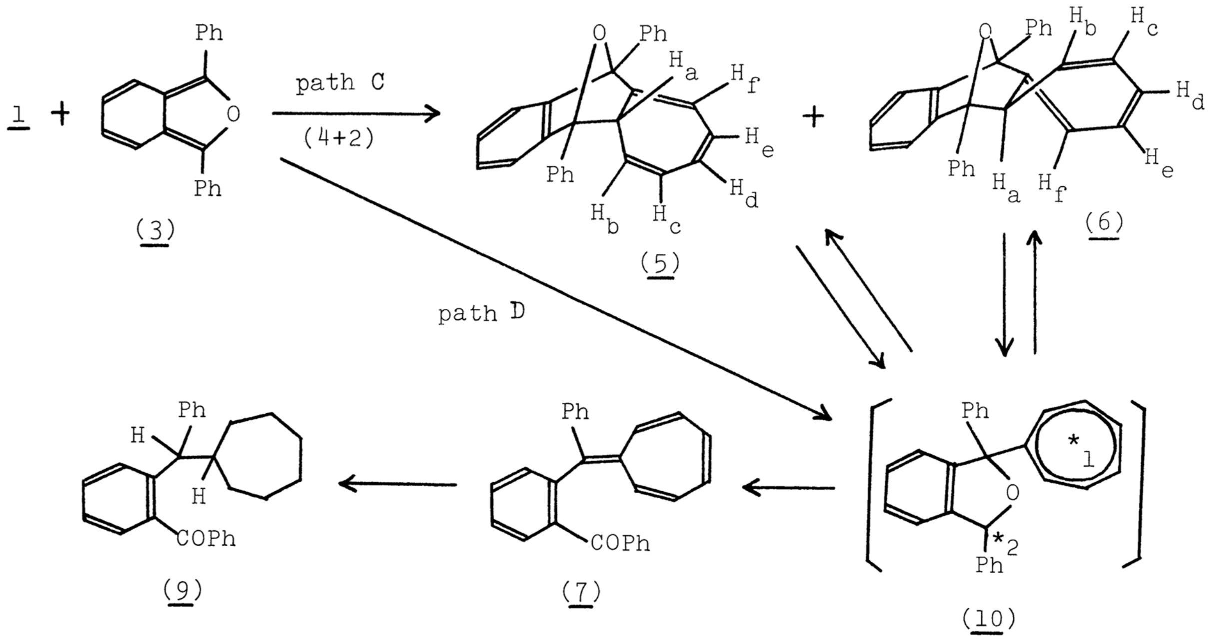
Addition reactions of cycloheptatrienylidene (1) with anthracene (2) and 1,3-diphenylisobenzofuran (3) gave (4+2) type adducts (4, 5, and 6) and a heptafulvene derivative (7). The reaction mechanisms for these cycloadditions are described.

Cycloheptatrienylidene (1) shows very low electrophilicity and adds only to electron deficient olefins as a nucleophilic singlet carbene,[1)] because of the contribution of a 6-π-electron system (1b).[1)] In these cases, spirocyclopropane derivatives are usually formed, but are sometimes accompanied by the secondary rearranged products possessing a methylenecyclobutane ring.[2)] In contrast to these reported reactions, we found a new type of cycloaddition of 1 with anthracene (2) and 1,3-diphenylisobenzofuran (3), where (4+2) type adducts (4, 5, and 6) were formed along with the thermally rearranged product 7. We wish to report an outline of these intriguing addition reactions.

When tropone tosylhydrazone sodium salt was heated in diglyme at 120°C for 15 min in the presence of 2.5 mol equiv. of anthracene (2), colorless prisms of 4 (mp 136°C) were obtained in 21% yield, accompanied by the evolution of a quantitative amount of nitrogen. The same reaction of tropone tosylhydrazone sodium salt with 2.5 mol equiv. of 1,3-diphenylisobenzofuran (3) gave colorless prisms of 5 (mp 190°C) and 6 (mp 178°C), and a red oil (7) in 20, 5, and 4% yields, respectively, together with a quantitative amount of nitrogen. The spectral properties of these products are as shown below.[3)] 4; UV (EtOH): 276 nm (log ε, 3.5); IR (KBr): 3030, 1600 cm^{-1}; NMR ($CDCl_3$) δ ppm: 2.46 (m, H_a), 4.47 (d, H_b), 4.63 (q, 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, Ph, 8H). Coupling constants (Hz): J_{ab}=3, J_{ac}=4, J_{ae}=2, J_{ce}=10. 5; UV (EtOH): 278 nm (log ε, 3.4); IR (KBr): 3030, 1600 cm^{-1}; NMR ($CDCl_3$) δ ppm: 3.68 (m, H_a), 4.75 (q, H_b), 5.85 (m, H_c), 6.13 (m, H_d), 6.20 (m, H_e, H_f), 7.0-7.8 (m, Ph, 14H). Coupling constants (Hz): J_{ab}=4, J_{ac}=2, J_{bc}=10, J_{cd}=5, J_{de}=11. 6; UV (EtOH): 278 nm (log ε, 3.7): IR (KBr): 3030, 1600 cm^{-1}; NMR ($CDCl_3$) δ ppm: 2.60 (m, H_a), 5.15 (q, H_b), 6.05 (m, H_c), 6.32 (m, H_d), 6.43 (m, H_e, H_f), 7.0-7.8 (m, Ph, 14H). Coupling constants (Hz): J_{ab}=4, J_{ac}=2, J_{bc}=10, J_{cd}=5, J_{de}=11. 7; UV (EtOH): 248 nm (log ε, 4.3), 332 (4.0); IR (oil): 1670 cm^{-1}; NMR ($CDCl_3$) δ ppm: 5.3-6.5 (m, 6H), 7.0-7.4 (m, Ph, 14H).


(1a)
(1b)
(1c)
1 +
(2)
path A
(4+2)
path B
Hd Hc He Hf Hg Hh Ha Hb
(4)
Ts
Ph Ph
(8)
H
*2
H
*1
(11)


1 +
Ph
O
Ph
(3)
path C
(4+2)
path D
O Ph Ha Hf He Hd Hc Hb Ph
(5)
+
O Ph Hb Hc Hd He Hf Ha Ph
(6)
Ph
*1
O
*2
Ph
(10)
Ph
COPh
(7)
H Ph H
COPh
(9)

The adducts 5 and 6 remained unchanged upon heating in diglyme under the same conditions as the addition reactions (120°C, 15 min), but under more drastic conditions (130°C, 25 hr), 5 gave 6 and 7 in 6 and 42% yields, respectively, although 5 was still recovered in 30% yield. Under the same conditions, 6 gave 5 and 7 in 2 and 20% yields, respectively, accompanied by the recovery of 6 in 68% yield. On the other hand, the adduct 4 was fairly stable toward heating, and was almost quantitatively recovered on heating at 150°C for 40 hr, but gave polymeric products upon heating at 180°C for 20 hr.

The structures of 4, 5, and 6 were determined to be (4+2) type adducts based on the double and triple resonance NMR spectra, and the good correlation of these NMR spectra with those of analogous compounds such as 8.[4] The stereochemistries of 5 (endo-adduct) and 6 (exo-adduct) were deduced from the chemical shifts of H_a and H_b of the two isomers. According to Dreiding models, H_a of 6 and H_b of 5 should be expected to show diamagnetic anisotropic effects from the o-disubstituted benzene moiety, resulting in high field shifts in their NMR spectra, compared to H_a of 5 and H_b of 6, respectively. The structures of 5 and 6 were further supported by the fact that the chemical shifts of H_a of 5 and 6 are consistent with that of the bridge-head proton of the endo-adduct of 1,3-diphenylisobenzofuran (3) with tropylidene (δ, 3.88 ppm)[5] and that of the H_a of 4, respectively, indicating that each pair of protons is located under almost the same chemical environment.

The structure of 7 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 region comparable to that of benzophenone. In addition, upon catalytic hydrogenation over Pd/C, 7 gave 9 in 96% yield by absorbing 4 mol equiv. of hydrogen. The structure of 9 was deduced from the following spectral properties. 9: UV (EtOH): 250 nm (log ε, 4.3); IR (oil): 1673 cm^{-1}; NMR (CCl_4) δ ppm: 1.3-2.4 (two broad peaks, 14H), 7.0-7.4 (m, Ph, 14H). The mechanism of the thermal reactions of 5 and 6 can be explained as proceeding via an ionic intermediate (10, $*_1=+$, $*_2=-$) which contains a stable tropylium cation moiety,[1,7] or a biradical intermediate (10, $*_1=*_2=\cdot$).

Recently, Jones et al. have pointed out the possibility of the reaction of 1 as an allene species (1c),[2] in addition to the well known nucleophilic additions as a singlet carbene (1a),[1] and they proved the isomerization of 1c to 1a.[2] However, the reverse rearrangement of the above, i.e., from the carbene form (1a) to the allene form (1c), has not been found, although 2,3-homocycloheptatrienylidene is known to rearrange to an allene form, 1,2,4,6-cyclooctatetraene.[8] From this point of view, it is interesting that the (4+2) type adducts 4, 5, and 6 were formed by the reactions of 1 with 2 and 3.

Two kinds of reaction paths can be proposed for the formation of 4, as shown in the scheme. One is a concerted (4+2) addition of the allene species (1c) with anthracene (path A), and the other is a two step addition via a tropylium cation (11, $*_1=+$, $*_2=-$) or a biradical intermediate (11, $*_1=*_2=\cdot$)(path B). Considering that anthracene is known to readily react as a 4-π-component in Diels-Alder reactions,[9] path A seems to be quite reasonable. The stability of the intermediate (11), however, does not allow one to neglect path B, where the intermediate (11) can be considered to be formed via the allene species (1c) as allenes are well known to add to olefins via multistep reaction mechanisms.[10] New types of reaction mechanisms (C and D) are possible for the addition of 1 with 3 which is known to be a strong diene in Diels-Alder reactions.[11] The thermal interconversion of the adducts 5 and 6, and the formation of 7 seem to support the interposition of the intermediate (10) (path D). However, the major formation of 5, which contains no less strain energy than that of 6 might suggest the contribution of a stabilization effect of a secondary orbital interaction in the transition state,[12] supporting the concerted (4+2) addition mechanism (path C). Thus it is difficult to decide between intermediate 1a or 1c in these reactions, and it is not illogical to consider the good possibility for these reactions to proceed via the allene form (1c).

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