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1-CYCLOHEPTATRIENYLIDENE-2-PHENYLETHYLENE AND ITS INTRIGUING DIMERIZATION REACTIONS[1]

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Treatment of 1-(2,4,6-cycloheptatrien-1-yl)-2-phenylacetylene (2) with DBU did not give the expected 1-cycloheptatrienylidene-2-phenylethylene (1) and instead its dimers (4, 5, and 6). Elucidation of the structure of the dimers 4 and 5, and a plausible mechanism of this facile dimerization reactions are described.

The chemistry of heptafulvenes[2] and 8-oxoheptafulvenes[3] has been studied in detail. However, cycloheptatrienylidenethylene (1) except for its dibenzo derivatives[4] has not been reported. Compound 1 consists of an allene and a heptafulvene moiety. Allenes usually behave as radical species in their dimerization reactions,[5] while heptafulvenes tend to possess tropylium cation type diporlar formulas,[2] for example 1a. It is therefore of interest to determine whether 1 behaves as an allene or a dipolar species. We report an attempted synthesis of 1-cycloheptatrienylidene-2-phenylethylene (3). Conditions expected to produce it instead afforded its dimers (4, 5, and 6). We conclude that the dimerization of 3 is unusually facile.

As the starting material for the sysnthesis of 3, 1-(2,4,6-cycloheptatrien-1-yl)-2-phenylacetylene (2) was prepared in a good yield by the reaction of 7-methoxycycloheptatriene with phenylethynylmagnesium bromide. Treatment of 2 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in ether afforded three crystalline products (4, 5, and 6; mp 157, 162, and 211° C) in 27, 43, and 4% yield, respectively.[6] Elemental analyses and mass spectra (M^+, 384; $C_{30}H_{24}$ for each of compounds) of 4, 5, and 6 indicated that each was a dimer of the expected allene 3. Attempted trapping of 3 with several dienophiles such as dimethyl acetylenedicarboxylate and cyclopentadiene failed to yield the expected adducts, and instead the dimer 4, 5, and 6 were formed in the yields and ratios identical to those in the absence of the dienophile. Treatment of 2 with DBU at -16° C resulted in the formation of the dimers in nearly the same ratios.

The double and triple resonance PMR spectra of 4 suggest the presence of both 1,7- and 7,7-disubstituted cycloheptatriene moieties. Treatment of 4 with tetracyanoethylene gave a 1:1 adduct[7] (7; mp 127° C) in which one of the cycloheptatrienes was converted into the norcaradiene. In the PMR spectrum of 7, a nuclear Overhauser effect was observed between H_1 and $H_{1'}$. Heating of 4 with DBU in benzene gave a mixture of two azulene derivatives (8 and 9; mp 124 and 167° C; ratio ca. 2:1) in 90% yield. The structure of 8 and 9 could be deduced from the PMR and UV-visible spectra.[7] The PMR spectrum of the cyclohexadiene moiety of 9 is nicely in accord with those of analogous cyclohexadiene compounds.[3a] The thermal derivation (300° C) of 8 from 9 also supports the correctness of the structure of 9. A plausible mechanism for the formation of 8 from 4 involves aromatization of the norcaradiene tautomer (4a) followed by 1,5-hydrogen shift. The formation of 9 can be explained either by the Cope rearrangement of 4a or by the corresponding radical process which involves the cyclohexadienyl radicals followed by 1,5-hydrogen shift.

The PMR spectrum of 5 suggests its symmetrical structure and the presence of 1,7-disubstituted cycloheptatriene moieties.[6] Heating of 5 above 120° C in degassed benzene solution afforded two 1,2-diphenylbenzocyclobutene derivatives (10 and 11; mp 215 and 207° C in 3:1 ratio; M^+, 384) in 22% yield.[8] Catalytic hydrogenation of 10 and 11 gave corresponding octahydro derivatives (12 and 13; mp 122 and 170° C; M^+, 392; $C_{30}H_{32}$). PMR spectra of either 10 or 12 show a sharp singlet at 4.43 or at 4.16 ppm (2H for each compound) close to that reported for trans-1,2-diphenylbenzocyclobutene,[9] and those of 11 or 13 show a singlet at 5.20 or at 4.94 ppm (2H), which correspond to that of cis-1,2-diphenylbenzocyclobutene,[9] respectively. The formation of 10 and 11 can be explained by double 1,5-hydrogen shifts in the cycloheptatriene moieties followed by aromatization and the benzocyclobutene formation. Reaction of 5 with 4-methyl-1,2,4-triazolin-3,5-dione gave a 1:2 adduct (14; mp 270° C) in 60% yield. The PMR signal of the methyl groups of 14 exhibits a sharp singlet at 2.84 ppm indicating the equivalence of two methyl groups. These facts support the correctness of structure 4 and 5 as the unsymmerical and symmetrical head-to-head dimers of 3, respectively.

In general, cycloheptatrienes afford tricyclo[3.2.2.$0^{2,4}$]nona-6-ene or 6,8-diene type adducts derived from their norcaradiene tautomers by the reactions with dienophiles.[10] Cycloheptatrienylacetylene 2 is rather unreactive under the dimer-forming reaction conditions in the absence of DBU, and at elevated temperature it gave tricyclo[3.2.2.$0^{2,4}$]nona-6-ene or 6,8-diene type adducts by the reactions with dienophiles. Even if the condensations took place between 2 and 3 under the dimer-forming reaction conditions, it is difficult to find rearrangement reaction pathways which lead to the dimers 4 and 5. Therefore, we believe that the dimers 4 and 5 are formed by the dimerization of the proposed allene intermediate 3. The facile dimerization of 3 is remarkable feature of the cycloheptatrienylidenylethylene system when compared with those of heptafulvenes or 8-oxoheptafulvenes. In those cases, the [8+8] or [8+2] type dimers were produced only under forcing conditions[3] or with only poor yields.[11] Analogous examples of such facile dimerizations are those of cyclopentadienone derivatives.[12] The dimerization mode of 3 reflects the properties of the heptafulvene moiety, because the dimerization took place at C_1 and C_8 positions, the most reactive positions of the heptafulvenes for cycloaddition reactions.[2] However, the facile dimerization tendency of 3 should depend on the allenic character. It is well known that the thermal self condensation of allenes occurs by radical mechanism.[5,13] Thus, the dimerization of 3 took place via a biradical intermediate 15 in which recombination of type a) resulted in the formation of 4 and type b) led to 5. Further studies are in progress to elucidate the stereochemistry of 4 and 5 as well as the dimerization mechanism of 3, and also structure determination of the dimer 6.

References and Notes

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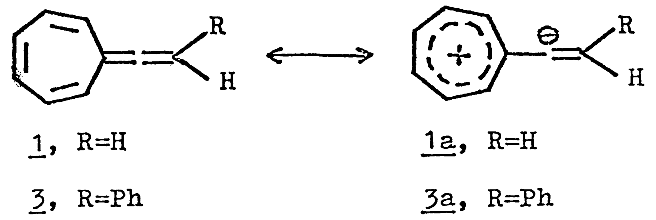
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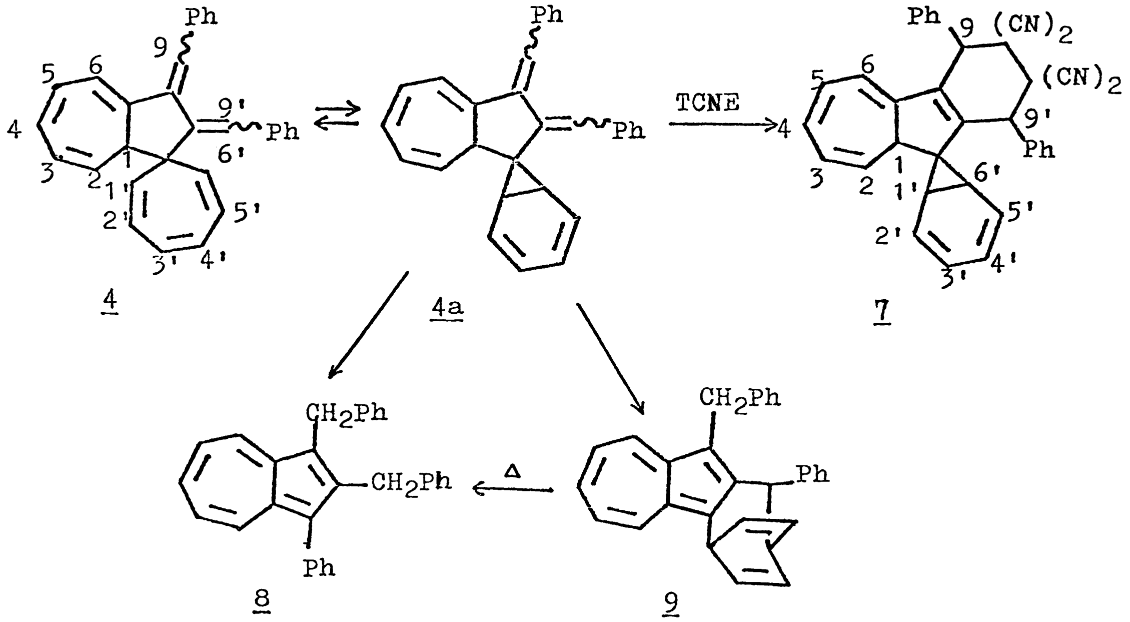
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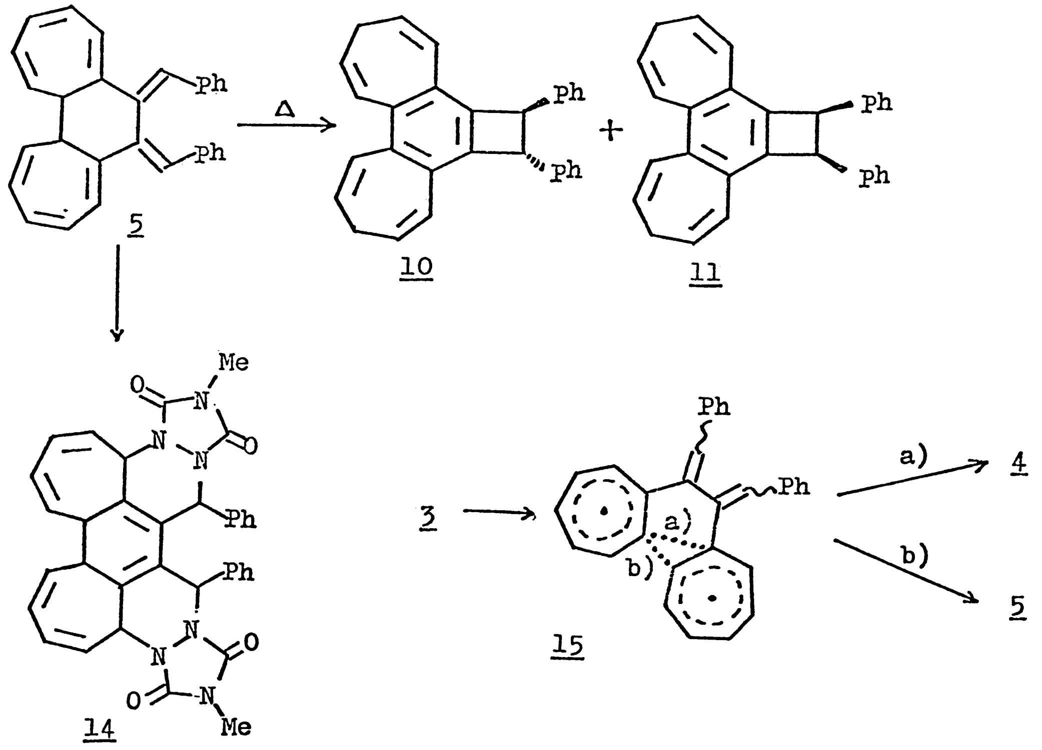
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a)
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6) Spectral data for 4 and 5. 4: PMR (δ, ppm in $CDCl_3$), 1.70 (H_1, d, J=5.5 Hz), 5.23 ($H_{2'}$, dd, 9 & 5.5 Hz), 5.44 ($H_{1'}$, d, 10 Hz), 5.75 ($H_{6'}$, d, 10 Hz), 5.9-6.1 (8H, m), 7.1-7.6 (12H, m); λ_{max}^{EtOH}, nm (log ε), 222.5 (4.14), 270 (3.72), 329 (3.79). 5: PMR (δ, ppm in $CDCl_3$), 2.50 (H_1, dd, 5 & 1.5 Hz), 5.59 (H_2, dd, 10 & 5 Hz), 6.26 (H_3, ddd, 10, 4, & 2 Hz), 6.3 (H_6, m), 6.5 ($H_{4,5,9}$, m, 6H), 7.1-7.6 (10H, m); λ_{max}^{EtOH}, nm (log ε), 221 (4.04), 268 (3.62), 322.5 (3.66).

7) Spectral data for 7, 8, and 9. 7: PMR (δ, ppm in $CDCl_3$), 1.70 (H_1, d, 5 Hz), 3.75 ($H_{1'}$, dd, 8 & 4.5 Hz), 4.34 ($H_{6'}$, dd 8 & 4.5 Hz), 4.49 ($H_{9'}$, d, 1.3 Hz), 4.68 (H_9, d, 1.3 Hz), 4.88 (H_2, dd, 9.5 & 5 Hz), 5.07 (1H, m), 5.8-6.4 (7H, m), 7.1-7.8 (10H, m); ν_{max}^{KBr}, 2250 cm^{-1}. 8: PMR (δ, ppm in CCl_4), 4.15 (2-benzyl, 2H, s), 4.26 (1-benzyl, 2H, s), 6.7-7.5 (18H, m), 8.07 (H_4, d, 9 Hz), 8.16 (H_8, d, 9 Hz); $\lambda_{max}^{cyclohexane}$, nm (log ε), 245 (4.44), 299 (4.73), 357 (3.82), 600 (2.44). 9: PMR (δ, ppm in CCl_4), 3.25 ($H_{1'}$, ddd, 6, 6, & 4 Hz), 3.37 (H_{1a}, d, 16.5 Hz), 4.00 (H_{1b}, d, 16.5 Hz), 4.10 ($H_{2'}$, d, 4 Hz), 4.56 ($H_{5'}$, dd, 6.5 & 6.5 Hz), 5.74 ($H_{8'}$, dd, 8 & 6 Hz), 6.16 ($H_{7'}$, dd, 8 & 6 Hz), 6.5-7.4 (15H, m), 7.91 (H_8, d, 9.5 Hz), 8.16 (H_4, d, 9.5 Hz); $\lambda_{max}^{cyclohexane}$, nm (log ε), 249 (4.25), 294 (4.78), 303 (4.79), 344 (3.65), 359 (3.72), 402 (2.99), 614 (2.40).

8) Spectral data for 10, 11, and 14. 10: PMR (δ, ppm in $CDCl_3$), 2.45 (2H, t, 7 Hz), 2.47 (2H, t, 7 Hz), 4.43 (2H, s), 5.91 (4H, m), 6.49 (2H, d, 10 Hz), 6.79 (2H, d, 10 Hz), 7.25 (10H, m); $\lambda_{max}^{cyclohexane}$, nm (log ε), 264.5 (4.76). 11: PMR (δ, ppm in $CDCl_3$), 2.49 (4H, t, 7 Hz), 5.20 (2H, s), 5.90 (4H, m), 6.47 (2H, d, 10 Hz), 6.79 (2H, d, 10 Hz), 6.94 (10H, m). 14: PMR (δ, ppm in $CDCl_3$), 2.84 (6H, s), 3.62 (2H, m), 5.52 (4H, m), 5.74 (2H, dd, 12 & 3 Hz), 6.07 (4H, s), 6.12 (2H, dm, 12 Hz), 6.8 (10H, m); ν_{max}^{KBr}, 1775 & 1710 cm^{-1}.

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