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1,2,4,6-CYCLOOCTATETRAENE, A NEW STRAINED CYCLIC ALLENE

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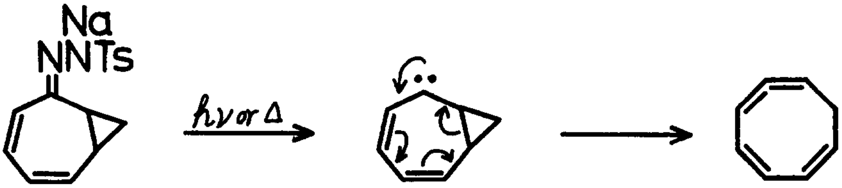
Cycloheptatrienylidene has been known to dimerize in the absence of olefins, giving heptafulvalene.[1] We wish here to report that bicyclo[5.1.0]-oct-3,5-dien-2-ylidene (2,3-homocycloheptatrienylidene) (2) undergoes immediate ring opening of the cyclopropane ring to produce 1,2,4,6-cyclooctatetraene (3), a new reactive, highly strained cyclic allene.

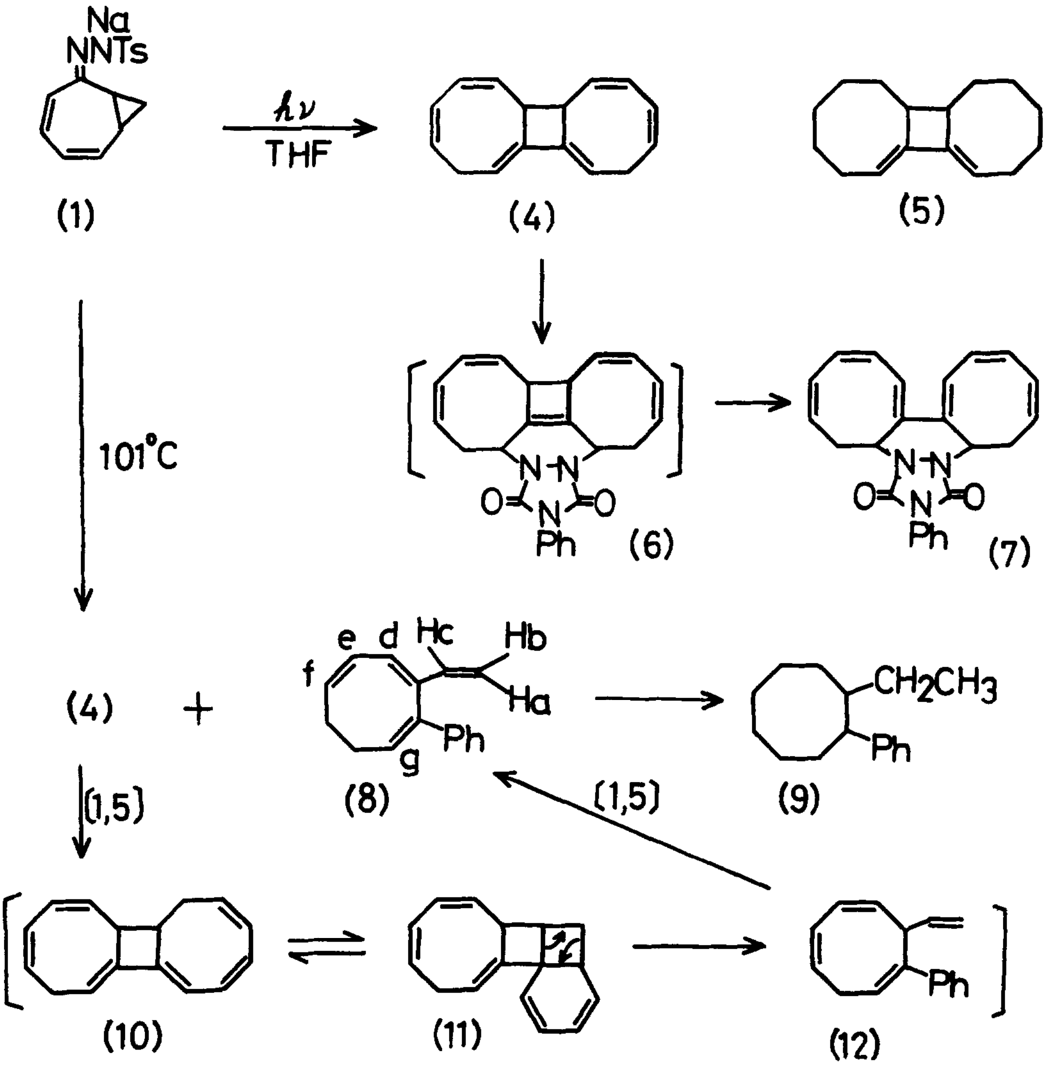


(1) (2) (3)

Photoirradiation of the sodium salt of 2,3-homotropone *p*-toluenesulfonylhydrazone (1)[2] in tetrahydrofuran for 3 hr evolved 85% theoretical amount of nitrogen and afforded a hydrocarbon (4) (pale yellow prisms, mp 72∿72.5°C, molecular formula=$C_{16}H_{16}$)[4] as the sole product in 70% yield. The compound (4) shows following spectral charactristics; IR (KBr), ν(C=C)=1620 cm^{-1}; UV (EtOH), λ_{max}nm (log ε)=218 (4.19), 248 sh(3.92), 259 (3.94), 268 sh(3.84); ^{1}H-NMR (100 MHz, CCl_4), δ_{ppm}=2.69 (4H, t, J=6.7 Hz), 3.37 (2H, br. s ($W_{1/2}$=7 Hz), 5.25-5.5 (4H, m), 5.57 (2H, dt, 6.7, 1.3 Hz), 6.0 (4H, m).

The ^{1}H-NMR spectrum indicates the absence of cyclopropane ring and suggests symmetric structure of the molecule. No observable coupling was found between the signals at δ=2.69 and 3.37 in the NMDR spectra, suggesting that these protons are not vicinal each other. The UV spectrum resembles that of the dimer of 1,2-cyclooctadiene (5).[5] The compound (4) smoothly reacted with N-phenyltriazoline-1,4-dione at room temperature to afford, probably via (6), the 1:1 adduct (7) (65%, mp 201-202°C); ^{1}H-NMR (100 MHz, $CDCl_3$), δ=2.4-2.9 (4H, m), 5.1-5.8 (6H, m), 5.9 (4H, narrow m), 6.5 (2H, narrow m), 7.4 (5H, m).

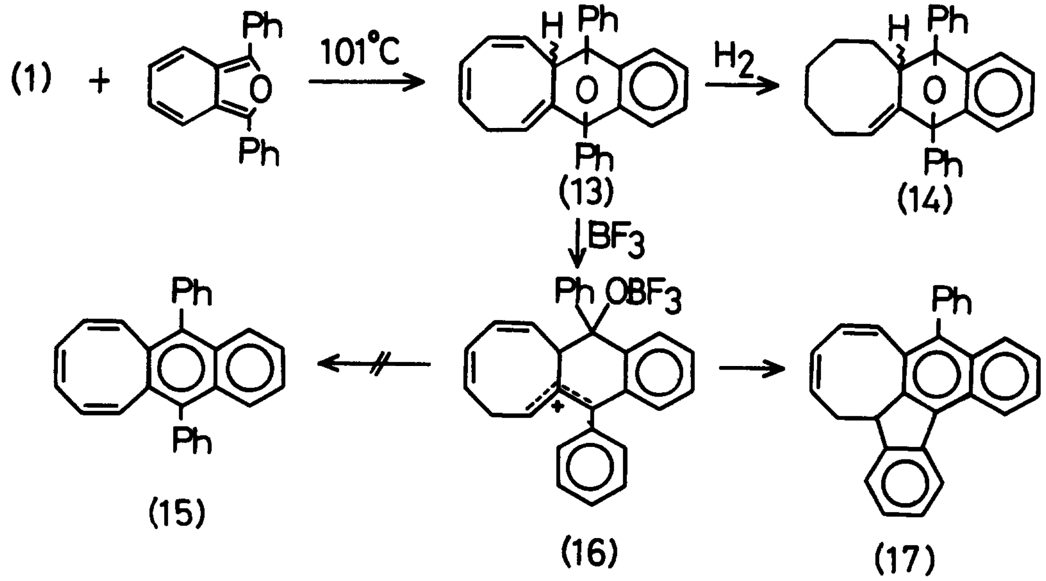
These results are in best accord with tricyclo[8.6.0.0^{2,9}]hexadec-2,5,7,11 13,16-hexaene for the structure of (4), which is a dimer of 1,2,4,6-cycloocta-tetraene.



Thermal decomposition of (1) in refluxing dioxane for 10 min afforded 2-phenyl-3-vinyl-1,3,5-cyclooctatriene (8) (43%) in addition to (4) (20%); ^{1}H-NMR-NMDR of (8) (100 MHz): δ=2.2-2.9 (4H, m), 4.72 (1H, dd, J=17.5, 2.8 Hz, Ha), 4.82 (1H, dd, 10.5, 2.8, Hb), 5.56 (1H, dt, 13.0, 3.5, Hf), 5.78 (1H, dd, 13.0, 4.8, He), 6.00 (1H, d, 4.8, Hd), 6.23 (1H, dd, 17.5, 10.5, Hc), 6.27 (1H, t, 7.5, Hg), 7.0-7.3 (5H, m, phenyl). Hydrogenation of (8) gave the octahydro-compound (9) whose NMR spectrum shows the presence of an ethyl group by exhibiting the methyl siganls at δ=0.83 as a triplet.

The compound (8) is formed by thermal rearrangement of (4) as evidenced by actual thermal transformation of the isolated (4) to (8) at 100°C. The rearrangement probably proceeds via (10), (11), and (12) as shown in the Scheme.

Thermal decomposition of (1) in the presence of diphenylisobenzofuran (1.0 equiv) afforded a stereoisomeric mixture of 1:1 Diels-Alder adducts (13) (the major adduct (13a): 48%, mp 161-161.5°C; the minor one (13b): 9%, mp 170-170.5°C). Partial hydrogenation of (13a) on platinum oxide led to the known compound (14) (mp 133-134°C, lit.[5b] mp 132-133°C). Photo-decomposition of (1) in the presence of excess cyclopentadiene also furnished a mixture of 1:1 Diels-Alder adducts. In the presence of furan, however, only dimer (4) was obtained.



On treatment with borontrifluoride etherate, (13a) did not afford diphenyl naphthocyclooctatetraene (15), but it underwent ring closure and dehydration to give quantitatively, probably via (16), the fluorene derivative (17); mp 185-186°C, ^{1}H-NMR ($CDCl_3$), δ=2.03 (1H, structured dd, J=19, 12 Hz), 3.23 (1H, structured d, 19), 4.54 (1H, dd, 12, 5.5), 6.0 (4H, m), 7.2-7.9 (13H, m).

The stereochemistry of dimer (4) has been as yet uncertain, although spontaneous electrocyclic ring opening of (6) may suggest trans configuration. 1,2-Cyclohexadiene has been reported to afford trans dimer.[6]

The formations of dimer (4) and Diels-Alder adducts with cyclic dienes indicate that the highly reactive species participating in the reactions is 1,2,4,6-cyclooctatetraene (3) which must have been formed by rearrangement of bicyclo[4.1.0]oct-3,5-dien-2-ylidene (2,3-homocycloheptatrienylidene) (2) initially generated by photochemical and thermal decomposition of (1).

References and Notes

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1) a) W. M. Jones and C. L. Ennis, J. Am. Chem. Soc., 89, 3069 (1967); 91 6391 (1969); b) T. Mukai; T. Nakazawa, and K. Isobe, Tetrahedron Lett., 565 (1968).

2) 2,3-Homotropone tosylhydrazone (mp 135-136°C) was prepared by reaction of 2,3-homotropone[3] with tosylhydrazine in pyridine (60°C, 12 hr, 82%); δ_{ppm} ($CDCl_3$)=0.7-1.8 (4H, m), 2.40 (3H, s), 5.3-6.3 (4H, m), 7.28 and 7.87 (A_2B_2). Treatment of the hydrazone with sodium hydride in tetrahydrofuran gave (1) as yellow solids.

3) a) J. D. Holmes and R. Pettit, J. Amer. Chem. Soc., 85, 2531 (1963); b) M. Oda, T. Sato, and Y. Kitahara, Synthesis, 721 (1974).

4) Satisfactory elemental analyses and/or mass spectra were obtained for all the new compounds here reported.

5) a) W. J. Ball and S. R. Landor, J. Chem. Soc., 2298 (1962); b) G. Wittig, H-L. Dorsch, and J. M. Schüller, Liebigs Ann., 711, 55 (1968). λ_{max}=250 (ε 8800), 259 (11,000), 269 nm (8300).

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