

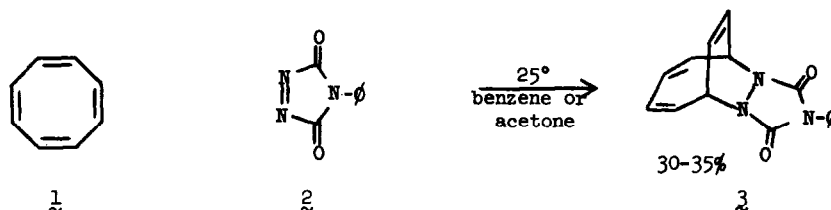
A 1,4-Cycloaddition Reaction of Cyclooctatetraene

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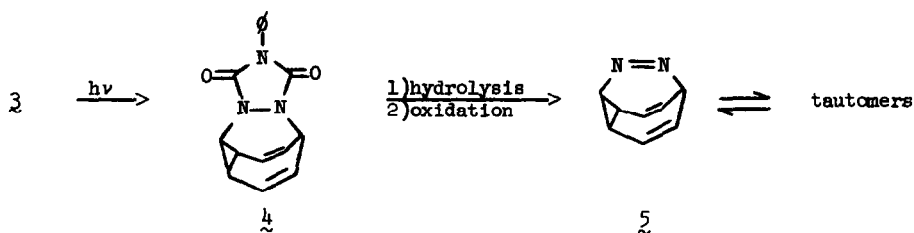
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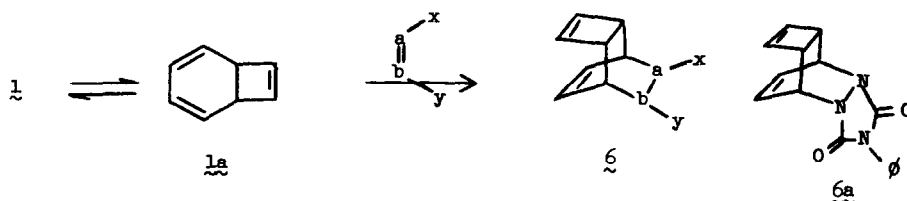
We have found that reaction of cyclooctatetraene (1) with 4-phenyl-1,2,4-triazoline-3,5-dione (2) at 25° affords 4-phenyl-2,4,6-triaza[5.4.2.0^{2,6}]tricyclo[trideca-8,10,12-triene-3,5-dione (3). The result is of considerable interest since examples of 1,4-cycloadditions



across 1 are virtually unknown¹ and because it may have bearing on the mechanism of addition of unsaturated hydrocarbons to azoesters. More significantly, 3 is a potential precursor to diazabullvalene, 5, a molecule of considerable synthetic and theoretical interest. Conversion of 3 to 4 has an ample precedent in Paquette and Barton's² preparation of methoxyazabullvalene.



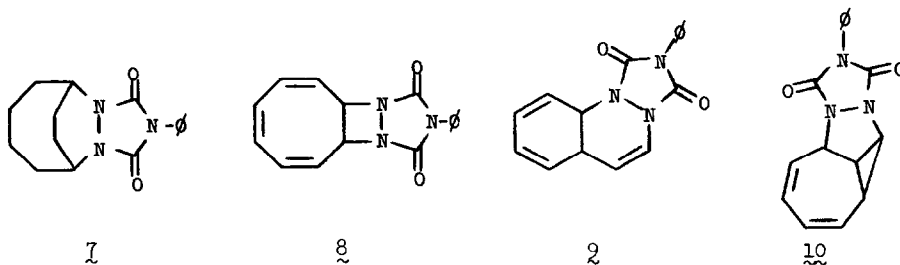
Previous studies of the reaction of cyclooctatetraene 1 with electron deficient olefins indicated that the reaction proceeded via the valence tautomer 1a.³ In fact, Cookson and co-



workers reported in 1967⁴ that reaction of 1 with 2 in dioxane at 100° afforded exclusively the expected adduct 6a in 32% yield. Reexamination of the reaction under these conditions revealed that the isomer 3 and 6a were formed in ca. a 1:1 ratio on the basis of the nmr spectrum of the crude mixture. Each was isolated in ca. 22% yield by chromatography on Florisil. Separate control experiments established that each of the pure isomers was completely stable under the reaction conditions. If the reaction is run at 25° in benzene or acetone, only traces (ca. 0.5%) of 6a could be detected. The variation of the product distribution with reaction temperature is of interest and will be studied in detail. The facile chromatographic separation of the isomers makes both compounds conveniently available for future investigations.

The structure assigned to the colorless, crystalline adduct, m.p. 204-5°,⁵ (3) rests firmly on spectral and chemical evidence. The nmr spectrum of 3 showed absorbances at δ (CDCl₃) 7.46 (m, 5H), 6.19 (m, 4H), 5.96 (q, 2H), and 5.14 (m, 2H). The infrared spectrum (KBr) had vinylic hydrogen stretching at 3.28 μ and a sharp doublet at 5.69 and 5.92 μ characteristic of the imide linkage. The ultraviolet spectrum (95% ethanol) showed no defined maxima but exhibited distinct shoulders at 245 m μ ($\epsilon = 4390$) and 280 m μ ($\epsilon = 1070$) as well as intense end absorption. The 70 eV mass spectrum of 3 employing direct ion source injection showed the following major peaks: m/e 279 (77, parent), 160(12), 131(16), 119(35), 118(47), 117(80), 104(25), 103(35), 91(100), 90(49), 78(38), and 77(22). Catalytic hydrogenation of 3 in ethyl acetate over platinum oxide resulted in the rapid uptake of three equivalents of hydrogen to yield the hexahydro derivative, 7, m.p. 180-182.5°. The nmr spectrum of 7 was characterized by complex multiplets centered at δ (CDCl₃) 7.5 (5H), 4.77 (2H), and 2.0 (12H).

The hydrogenation data and mass spectral isotopic abundance measurements are, however, also consistent with structure 8, and a double resonance experiment was required to eliminate this possibility. Irradiation of the aliphatic proton multiplet at 5.14 δ led to collapse of the two proton quartet at 5.96 δ into a sharp singlet; the absence of coupling between the



protons at 5.96 δ and the other olefinic hydrogens is only consistent with structure 3. Mechanistically less probable adducts such as 9 and 10 are excluded by the molecular symmetry revealed by the nmr spectrum and by the double resonance experiment.

We are currently examining both the mechanism of formation of 3 and the possibility of its conversion to diazabullvalene. The acetone photosensitized irradiation of 3 does yield a photoproduct whose spectral properties are consistent with those anticipated for 4.

ACKNOWLEDGEMENT

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REFERENCES

1. The only other reagents that have reacted with 1 in this manner are benzyne (E. Vedejs, Tetrahedron Letters, 2633 (1968)), chlorosulfonylisocyanate² and cyanonitrene (A. G. Anastassiou, J. Am. Chem. Soc., 90, 1527 (1968)).
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4. R. C. Cookson, S. S. H. Giliani and I. D. R. Stevens, J. Chem. Soc. (C), 1905 (1967).
5. Satisfactory elemental analyses were received for all new compounds; m.p.'s are corrected.