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ALL-cis CYCLONONA-1,3,5,7-TETRAENE.
SYNTHESIS; THERMAL AND PHOTOCHEMICAL REORGANIZATION.

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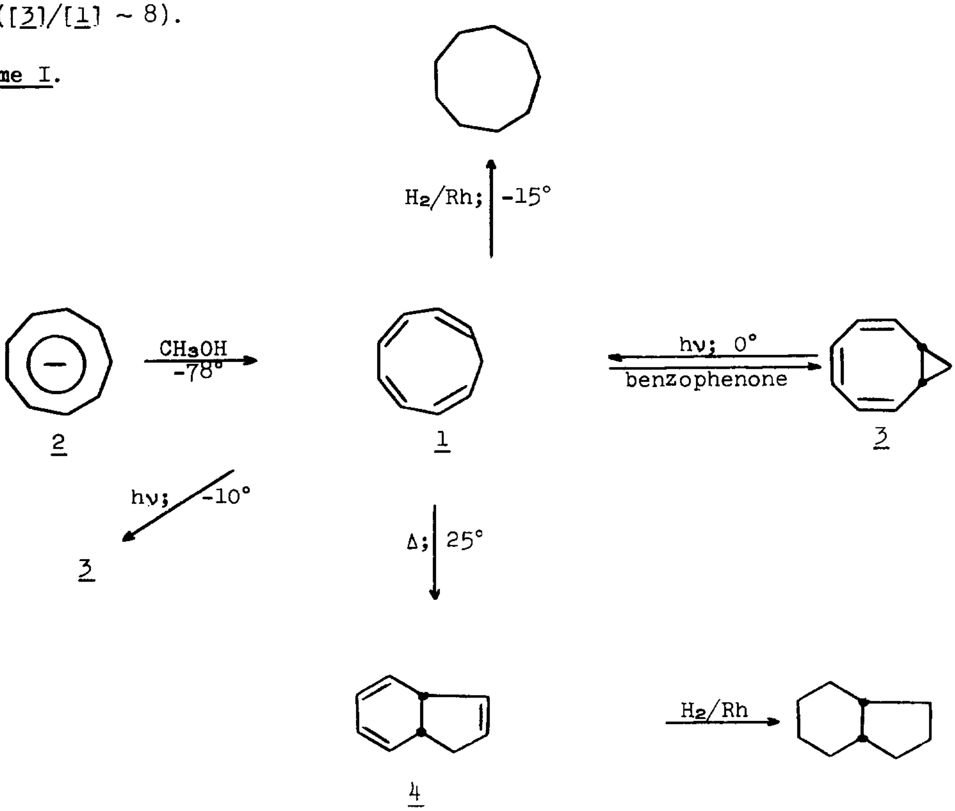
Owing to our recent synthesis of N-carbethoxylazonin (1) and oxonin we became quite interested in the title compound (all-cis CNT) 1 as an ideal classical-polyenic model. Furthermore, our recent description of the various reorganization pathways available to both ground and excited state CNT, (3) coupled with subsequent experimental information concerning the possible intermediacy of this tetraene in the thermal rearrangement of various 9-substituted bicyclo[6.1.0]nona-2,4,6-trienes, (4a-c) provided additional incentive for isolating 1. We presently report on the synthesis, isolation and bond reorganization of this coveted substance.

The synthesis in question was executed by the two distinct procedures shown in Scheme I. Among these, low temperature protonation of cyclononatetraenide (5a,b) 2 is decidedly the method of choice as it furnishes pure 1 in up to 50% yield. The yellow, mobile liquid obtained in this fashion displays spectral characteristics anticipated of all-cis CNT. Thus, it exhibits nmr signals ($CDCl_3$; ca., -30°) at τ 4.21 (8 H, singlet) and τ 6.90 (2 H, triplet) its uv spectrum ($\lambda_{max}^{C_6H_{14}}$ 205 nm, ($\varepsilon > 5000$), 248 (sh) ($\varepsilon \sim 2500$)) is, as expected, not unlike that of cyclooctatetraene (COT). (6) Definitive chemical proof that the compound in question is indeed cyclononatetraene obtains from its low-temperature (-15°) catalytic (Rh-C) hydrogenation to cyclononane. (7)

The alternate method of synthesis of 1 was designed primarily on the basis of orbital symmetry which permits interconversion of electronically excited 1 and 3. (3) Indeed, through-"Pyrex"irradiation of a cold (0°) ethereal solution of 3 and benzophenone with a "Hanovia" light source leads exclusively to 1 as indicated by immediate nmr analysis of the cold photolysate. Generation of 1 in this fashion is of limited synthetic value however as the reaction appears to rapidly reach a photostationary state consisting predominantly of 3 ([3]/[1] $\sim$ 8).

Scheme I.



At ambient temperature, 1 undergoes rapid bond relocation to generate *cis*-8,9-dihydroindene 4. This compound, shown (gc) to constitute over 97% of the thermolysis mixture, was isolated gas-chromatographically and characterized through direct comparison (ir) with an authentic sample. (8) Additionally, catalytic hydrogenation of the thermolysate produced *cis*-hydrindane. Contrasting the thermal reorganizagion, direct, through-"Pyrex" illumination of a cold (-10°) ethereal solution of 1 with a "Hanovia" light source leads, cleanly and exclusively, to 3. Under these conditions the tetraene 1 is entirely consumed in *ca*. 1 hr.

Preliminary observations concerning thermal cycloaddition reactions of CNT point to an overall reluctance of this molecule to react by way of its monocyclic arrangement. For example, treatment of 1 with tetracyanoethylene at or below 0°C leads solely to the known (mp., ir.) (5a) tetracyanoethylene adduct of *cis*-8,9-dihydroindene. All-*cis* CNT does however react quite readily with 4-phenyl-1,2,4-triazoline-3,5-dione to yield a single major product, mp. 184-186°, with an nmr spectrum (complex, multiplets at τ 2.5-2.7 (5 H), τ 3.6-5.1 (8 H), τ 6.8-7.3 (1 H), τ 7.8-8.3 (1 H)) solely consistent with a structure containing a monocyclic hydrocarbon segment. Full structural characterization of this substance is currently in progress in our laboratories.

Finally, we briefly point that all structural reorganizations of the C_9H_{10} system described herein occur in a strictly specific fashion along paths entirely prescribed by "frontier" orbital symmetry. (3) We are continuing our work in this area.

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REFERENCES

(1) A. G. Anastassiou and J. H. Gebrian, *J. Am. Chem. Soc.*, **91**, 4011 (1969).

(2) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903 (1969).

(3) A. G. Anastassiou, *J. Am. Chem. Soc.*, **90**, 1527 (1968).

(4) (a) S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.*, **91**, 1239 (1969);
(b) P. Radlick and W. Fenical, *J. Am. Chem. Soc.*, **91**, 1560 (1969);
(c) S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.*, **91**, 0000 (1969).

(5) (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964);
(b) E. A. LaLancette and R. E Benson, *J. Am. Chem. Soc.*, **87**, 1941 (1965).
Both groups reported that protonation of 2 leads to 8,9-dihydroindene as the sole isolable product. Furthermore, attempts to isolate CNT in this fashion were described as unsuccessful.[5b]

(6) Undoubtedly, 1 is puckered. The most stable geometry suggested by a "Dreiding" molecular model is one which possesses a two-fold rotating axis of symmetry containing the unique tetrahedral carbon and bisecting the remote C-C bond. In this arrangement the relative disposition of the various double bonds is not unlike that present in "tub"-shaped COT.

(7) Identified through direct infrared comparison with authentic material. A. T. Blomquist, L. H. Liu and J. C. Bohrer, J. Am. Chem. Soc., 74, 3643 (1952).

(8) We thank Dr. Maitland Jones, Jr. for providing us with the infrared spectrum of authentic 4.