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THE *exo,exo*-11,12-DIAZATETRACYCLO[4.4.2.$0^{2,5}$.$0^{7,10}$]DODECA-3,8,11-TRIENE SYSTEM[1]

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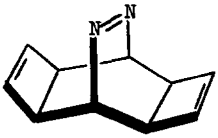
THERE has been much recent interest in the preparation of [10]annulenes, the simplest ($4n + 2$) π-electron homologs of benzene. However, synthetic entry to such elusive substances has been gained to this time only by photochemical or thermal valence bond isomerization of 9,10-dihydronaphthalenes.[2] We have been engaged in developing new synthetic approaches to cyclodecapentaenes and wish at this time to call attention to the *exo,exo*-11,12-diazatetracyclo[4.4.2.$0^{2,5}$.$0^{7,10}$]dodeca-3,8,11-triene system (1). This molecule contains an azo linkage and ten appropriately disposed (CH) units and is therefore an attractive potential precursor of [10]annulene. We describe here the preparation of the first member of this class of azo compounds and present a preliminary account of its thermal behavior.



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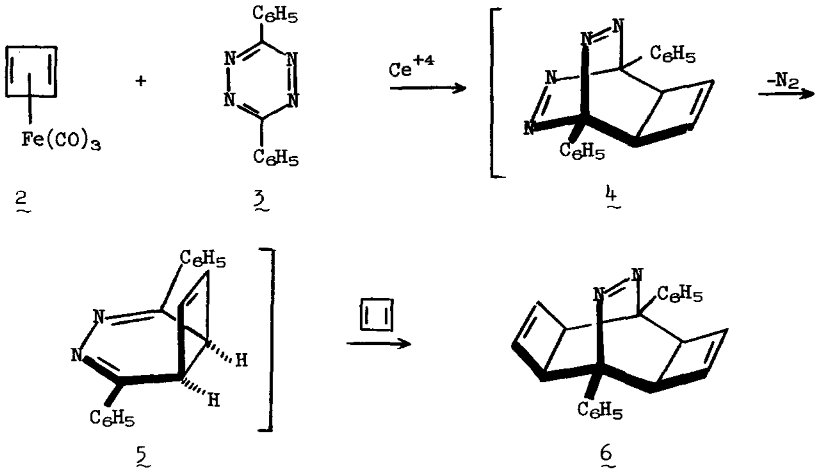
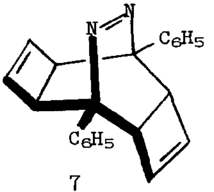
Gradual addition of powdered ceric ammonium nitrate to a cold (0°) stirred acetone solution of cyclobutadieneiron tricarbonyl (2) and diphenyl-*s*-tetrazine (3) results in the production of adduct 6 (77% yield) derived from one equivalent of tetrazine and two of cyclobutadiene. This tetracyclic azo compound (6)[3] is reasoned to be the result of initial Diels-Alder condensation of cyclobutadiene to 3, facile loss of nitrogen from 4 (a symmetry-allowed ${}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ bond cleavage),[4] and addition of a second mole of cyclobutadiene to 5. Since 6 is the only product formed, irrespective of the relative proportion of tetrazine present, it appears that 5 (the bicyclic valence tautomer of a 1,2-diazocine) is more reactive toward



cyclobutadiene than 3.

The exo,exo configuration of 6, assigned to conform with symmetry-controlled secondary orbital interactions operative in the transition state for cycloaddition to 5,[5] was supported by its nmr spectrum which fully substantiated a highly symmetrical structure: $\delta_{TMS}^{CDCl_3}$ 7.40-7.95 (m, 10, aromatic), 5.91 (s, 4, vinyl), and 3.45 (s, 4, allylic). Because the steric bulk of the cyclobutene ring in 5 opposes the approach of cyclobutadiene from the top surface, this four-membered ring necessarily becomes cis to the developing azo linkage. The endo,exo isomer of 6 (7) would be expected to exhibit an nmr spectrum displaying two separate



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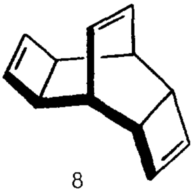

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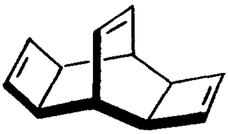

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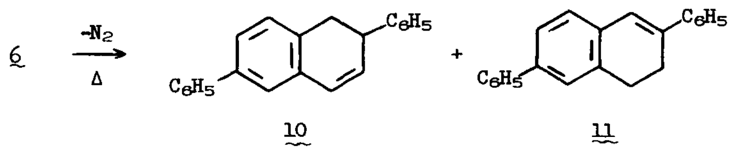
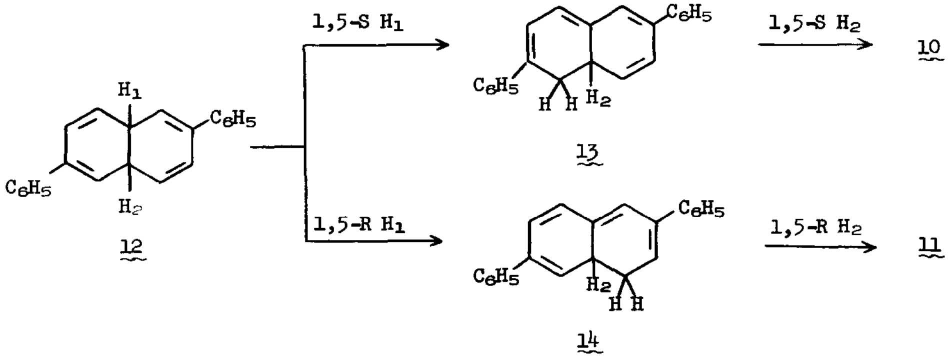
cyclobutene regions, by analogy to the spectral properties of 8;[6] exo,exo isomer 9, like 6, shows a highly symmetrical spectrum.[6]

Thermal decomposition of 6 in refluxing o-dichlorobenzene (30 min) leads to the production of 10[3] and 11[3] in yields of 78.5% and 8%, respectively. The structures of these hydrocarbons were secured on the basis of their ultraviolet spectra[7] and unequivocal synthesis from 2,6-diphenyl-4-tetralone.[8] Control experiments showed that interconversion of 10 and 11 clearly is not operative under the thermolysis conditions; however, prolonged heating of the mix-



ture does result in oxidation of both 10 and 11 to 2,6-diphenylnaphthalene.

While the nature of the phenyl substitution in 10 and 11 virtually requires the transient occurrence of a 1,6-diphenylcyclodecapentaene, isolation of the less conjugated dihydronaphthalene 10 as the major product (ratio of 10/11 produced is 9.8) demonstrates that the subsequent rearrangement of this [10]annulene intermediate is not controlled by the relative stabilities of these two unsaturated hydrocarbons. This result is rationalizable in terms of different rates of thermal [1,5] sigmatropic hydrogen shifts in 12, the bicyclic valence tautomer of the [10]annulene. Two such suprafacial migrations in 12 are possible; whereas movement in the counterclocksise direction (1,5-S shift) leads to 13, 1,5-R shift affords 14. Such competitive processes would be expected to be controlled by stabilization factors in 13 and 14 if the respective transition states reside close to product. Since 13 is more extensively conjugated than 14, its rate of production would be faster in view of the anticipated differences in activation energies for the two rearrangements. Further progress along these two reaction coordinates requires that H_2 migrate in the same sense as H_1 in each instance, if the benzenoid character in 10 and 11 is to be established.[9]



The 12 → 10 and 12 → 11 rearrangements thus occur under considerable control by the developing systems of extended conjugation. Realization that such a complex set of migrations is governed by electronic considerations of this type should now serve to further the predictive power of orbital symmetry relationships, particularly in those situations where two or more alternatives are possible.

Further extensions of the thermal degradation of 11,12-diazatetracyclo[$4.4.2.0^{2,5}.0^{7,10}$]-dodeca-3,8,11-trienes as an approach to hitherto unknown cyclodecapentaenes, together with the photochemistry of these polycyclic azo compounds, will be reported subsequently.

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REFERENCES AND NOTES

(1) Appreciation is expressed to the Army Research Office (Durham) for financial support of this research.

(2) (a) M. Avram, C. D. Nenitzescu, and E. Marica, *Ber.*, **90**, 1857 (1957); (b) R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind.* (London), 21 (1961); (c) E. Vogel, W. Meckel, and W. Grimme, *Angew. Chem.*, **76**, 786 (1964); (d) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963); (e) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963); (f) J. J. Bloomfield and W. T. Quinlin, *J. Am. Chem. Soc.*, **86**, 2738 (1964); (g) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); (h) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

(3) Elemental analyses, carried out on all new substances described, were within satisfactory limits (± 0.3%).

(4) Ready loss of nitrogen from related tetraazanorbornadienes has been previously observed: (a) R. A. Carboni and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 4342 (1959); (b) M. Avram, I. G. Dinulescu, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, **95**, 2248 (1962); (c) J. Sauer and G. Heinrichs, *Tetrahedron Lett.*, 4979 (1966); (d) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967).

(5) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

(6) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, in press.

(7) For **10**: $\lambda_{max}^{CH_3OH}$ 248 nm (ε 56,100); for **11**, $\lambda_{max}^{CH_3OH}$ 260 (ε 30,800) and 317 nm (ε 33,700).

(8) C. C. Price and A. J. Tomisek, *J. Org. Chem.*, **7**, 517 (1942); *J. Am. Chem. Soc.*, **65**, 439 (1943). The complete details of these transformations will appear in a later full paper.

(9) The precise stereochemistries of **12** and the 1,6-diphenylcyclodecapentaene intermediate are not known. We propose, however, that the arguments concerning the 1,5-hydrogen shifts are not strictly dependent upon the *cis* or *trans* nature of the C_9C_{10} ring fusion in **12**. This would require that the sigmatropic shifts occur more rapidly than hydrogen transfer [see W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **89**, 4534 (1967)]; since only **10** and **11**, but no 1,6-diphenylnaphthalene was observed after short reaction times, this speculation is considerably strengthened.