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STEREOCHEMISTRY OF A THERMAL REARRANGEMENT IN THE $(CH)_{12}$ SERIES. ESTABLISHMENT OF THE SUPRAFACIAL NATURE OF A [1,5] CARBON MIGRATION

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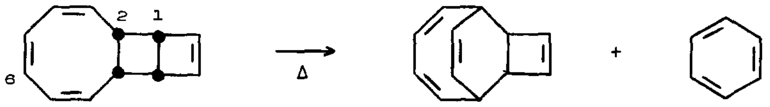
Heating of cis,syn,cis-tricyclo[8.2.0.0^{2,9}]dodeca-3,5,7,11-tetraene (1) at 120° for 24 hr has been reported to result in the formation of equal amounts of benzene and hydrocarbon 2.[1] The stereochemistry of 2 was not determined. The thermal rearrangement of 1 to 2 formally involves the [1;5] migration of C-1 from C-2 to C-6, a sigmatropic change which, if concerted, would be restricted for reasons of orbital symmetry conservation to the use of a suprafacial orbital at the migration terminus.[2] However, while the preferred conformation of 1 can be considered to resemble closely the tub structure 3, this arrangement does not lend itself geometrically to such a concerted bond migration. Also, although alternative tub conformation 4 would not suffer from such a stereochemical disadvantage, the non-bonded interactions present in 4 suggest, a priori, that this structural arrangement might be energetically inaccessible. Consequently, the bond reorganization in 1 could be occurring in non-concerted fashion via diradical 5 which would cyclize to give either 6 or 7. The ease



1 2

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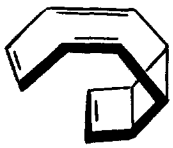

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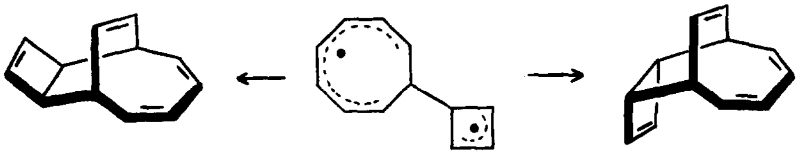
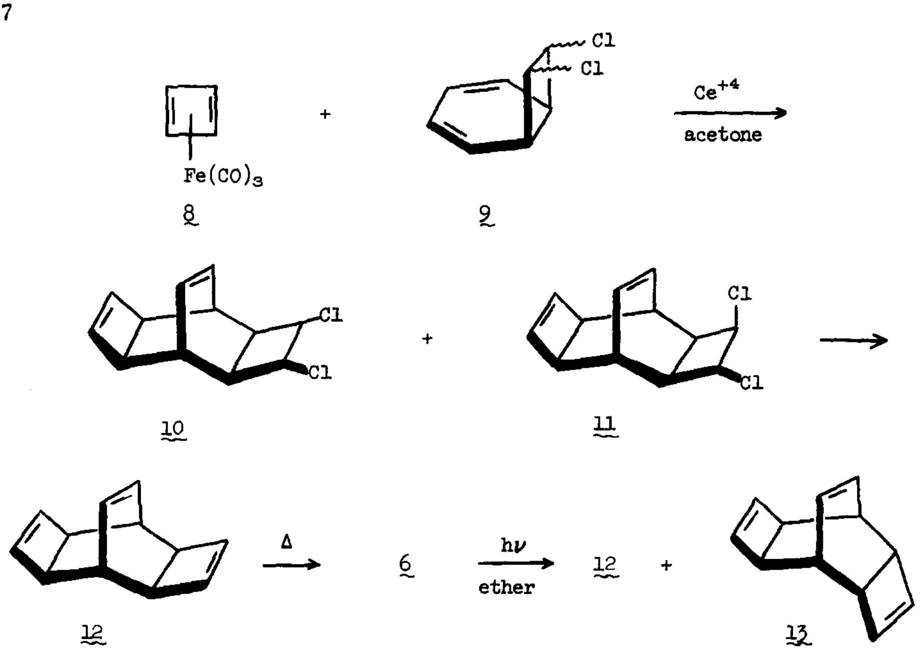
with which several bonds in 1 are ruptured has already been noted;[1,3] in addition, the con-



6 5 7

ditions required for the 1 → 2 rearrangement can be construed to be somewhat more vigorous than that demanded by a concerted intramolecular [1,5] shift, although very few examples of such a carbon migration are known.[4] On the other hand, Schröder's observation that 2 is a single isomer is difficult to rationalize on the basis of intermediate 5, since energy considerations disclose that formation of 6 and 7 from this diradical should be equally facile. In the present paper, we wish to report that thermolysis of 1 leads uniquely to 6 and to describe briefly the photoisomerization of this $(CH)_{12}$ polyolefin.

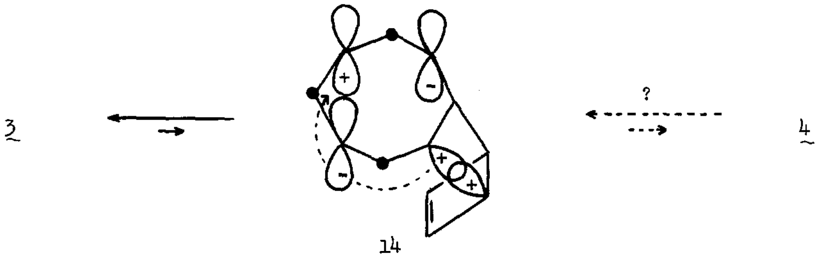
When powdered ceric ammonium nitrate is slowly added to a solution of cyclobutadieneiron tricarbonyl (8) and a cis,trans mixture of 7,8-dichlorobicyclo[4.2.0]octadiene (9)[5] in acetone at room temperature, the Diels-Alder adducts 10 and 11 are formed in a combined yield of 52%. Column chromatography of the product on neutral alumina results in ready separation of cis-dichloride 10,[6] mp 131-132° [$\delta^{CDCl_3}_{TMS}$ 2.5-3.0 (m, 6H, methine protons), 4.1-4.25 (m, 2H, >CHCl), 5.87 (s, 2H, cyclobutene protons), and 6.05-6.25 (broadened triplet, 2H, vinyl protons)] from the trans isomer 11,[6] mp 94-95° [$\delta^{CDCl_3}_{TMS}$ 2.5-3.1 (m, 6H, methine protons), 4.1-4.70 (m, 2H, >CHCl), 5.87 (s, 2H, cyclobutene protons), and 5.9-6.4 (m, 2H, vinyl protons)]. The stereochemical configurations of 10 and 11 are in accordance with established precedence,[7] symmetry-controlled secondary orbital interactions operative in the transition states for cycloaddition to 9,[8] and spectroscopic evidence. For example, it follows that because the dichlorocyclobutane moiety in 9 sterically inhibits the approach of cyclobutadiene from the top surface, this halogenated ring necessarily becomes cis to the developing ethylene bridge. Additionally, the exo orientation of the cyclobutene ring was confirmed by dechlorination of 10 and 11 with sodium phenanthrene in THF solution (69% yield). The resulting hydrocarbon (12), mp 25.5-26.5°,[6] displays a highly symmetrical nmr spectrum ($CDCl_3$) consisting inter alia of a single sharp singlet at δ 5.84 due to the four equivalent cyclobutene protons. The exo,exo stereochemistry of 12 is further substantiated by comparison with the spectrum of 13 (see below).



Pyrolysis of 12 at 500° and 15 mm readily affords the isomeric $(CH)_{12}$ hydrocarbon 6, which proved to be identical in all respects with the thermal rearrangement product of 1.[9] Ultraviolet irradiation (Hanovia 450w light source) of a 1% solution of 6 in ether for approximately 3 hr at room temperature gives 12 and 13 in equal amounts.[10,11] The nmr spectrum of 13 displays, inter alia, two cyclobutene singlets at δ 6.27 and 5.62. This photorearrangement affords additional confirmation of structure 6 since 12 would not be expected from the irradiation of 7.

Partial decomposition of such an equimolar mixture of 12 and 13 at 500° revealed that 12 undergoes thermal rearrangement slightly more rapidly than 13. Thermal rearrangement of pure 13 gave only 6, indicating that the endo cyclobutene ring in 13 is cleaved exclusively under these conditions.

The identification of pyrolysis product 2 as stereoisomer 6 requires that the thermal rearrangement of 1 be necessarily suprafacial. It may well be that the transition state for this sigmatropic change is not severely constrained as in 4; rather, the unfavorable repulsion interactions present in 4 may be balanced against the internal angle strain that develops as the cyclooctatriene ring attains planarity as in 14. In this conformation, the pentadienyl system required for the 1,5-suprafacial bonding is capable of maintaining the approximate co-



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planarity necessary for application of the orbital symmetry rules. In any case, the stereochemical outcome of the rearrangement of **1** denotes once again the considerable importance of orbital symmetry control in a polyene where a multitude of alternative bond rearrangements are possible.

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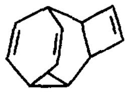
References

1. G. Schröder and W. Martin, Angew. Chem., **78**, 117 (1966); Angew. Chem. Intern. Ed. Engl., **5**, 130 (1966).
2. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., **87**, 2511 (1965).
3. G. Schröder, W. Martin, and H. Röttele, Angew. Chem., **81**, 33 (1969); Angew. Chem. Intern. Ed. Engl., **8**, 69 (1969).
4. J. A. Berson, Accts. of Chem. Res., **1**, 152 (1968).
5. R. Huisgen, G. Boche, W. Hechtl, and H. Huber, Angew. Chem., **78**, 595 (1966); Angew. Chem. Intern. Ed. Engl., **5**, 585 (1966).
6. Satisfactory elemental analyses (± 0.3%) were obtained for all new compounds.
7. For a review of cyclooctatetraene chemistry, see G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.
8. R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc., **87**, 4388 (1965).
9. Spectral data for **6** may be found in reference 1.
10. G. Schröder and W. Martin have also observed this photorearrangement [unpublished results mentioned in G. Schröder and J. F. M. Oth, Angew. Chem. Intern. Ed. Engl., **6**, 414 (1967)]; however, stereochemical assignments were not made by these authors since the stereochemistry of **6** was unknown to them.
11. In contrast, irradiation of **6** under triplet conditions (acetone solution) affords **i**:



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