Tetrahedron Letters No.19, pp. 1359-1362, 1965. Pergamon Press Ltd.
Printed in Great Britain.

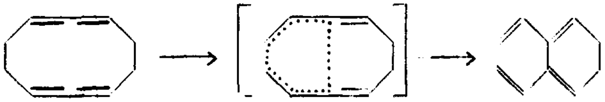
THERMAL REARRANGEMENTS IN 10-CARBON CYCLIC ALLENES

John F. Harris, Jr.*

Institut für Organische Chemie der Universität Köln

(Received 1 March 1965; in revised form 18 March 1965)

It was shown earlier(1) that 1,2,6-cyclononatriene (a 1,5-hexadiene in which one of the double bonds is part of an allenic system) undergoes a Cope-type rearrangement at 140° to give 2,3-divinylcyclopentene. It has now been found that analogous rearrangements occur in 10-membered rings containing the 1,5-hexadiene system where one or both of the double bonds is incorporated in an allenic function. Thus, 1,2,6,7-cyclodecatetraene (I)(2) undergoes a rearrangement at 300° (0.05 mm.) in a flow system to give 2,3-divinyl-1,3-cyclohexadiene (II) in virtually quantitative yield.(3,4)



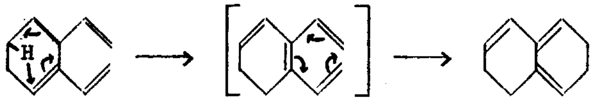
I

II

---

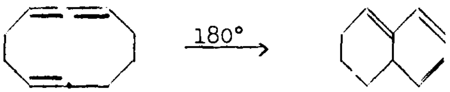
* Present address: Central Research Dept., E. I. du Pont de Nemours and Co., Wilmington, Delaware.

II (b.p. 66°/12 mm.) is an easily polymerized, oxygen sensitive compound possessing a λ_{max} at 232.5 mμ, ϵ = 13,000. The NMR spectrum contains two groups of resonances, one in the vinyl proton region and one in the methylene proton region in an intensity ratio of 2:1. By virtue of a plane of symmetry, there are only six different kinds of hydrogen atoms in the molecule, and the spectrum is rather simple. The exocyclic vinyl proton resonances occur as three quadruplets (an ABC pattern) at τ = 3.4-5.6. The ring vinyl proton occurs at τ = 4.04 and is only weakly split. The methylene protons occur as a pair of doublets centered at τ = 7.90. Further support for the assigned structure II comes from the infrared spectrum and from catalytic hydrogenation (Pt) in which 4 moles of hydrogen are taken up to give cis and trans-1,2-diethylcyclohexane. At higher temperatures, II undergoes further rearrangement with the formation of a tetrahydronaphthalene, presumably via a 1,5-hydrogen shift followed by ring closure, to give III or some isomer of III:



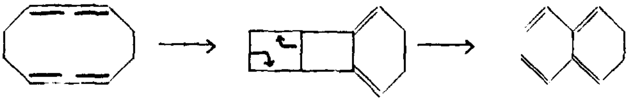
III

1,2,6-Cyclodecatriene (IV; b.p., 47.5-48.5°/2.0 mm.; n_D^{20}, 1.5253) also undergoes a rearrangement at 180° in a static system to give 2,3-divinylcyclohexene (V) (b.p. 57°/13 mm.) in virtually quantitative conversion:



IV V

We prefer to picture these rearrangements as occurring via the mechanism generally assumed for Cope rearrangements,(5) although with the data thus far in hand it is not possible to exclude a mechanism involving cycloaddition to give a four-membered ring intermediate:



The driving force for these rearrangements is no doubt largely the energy released in the conversion of the allenic linkages to conjugated diene functions. Release of ring strain may also be a factor, although models indicate that these 10-membered ring allenes can assume relatively strain-free conformations. Models also show that the reacting multiple bonds can be rather close to each other, thus facilitating assumption of the transition state geometry.

Acknowledgements: The author expresses his gratitude to Professor Emanuel Vogel who suggested this research and with whose collaboration it was carried out. Support from the John Simon Guggenheim Memorial Foundation is gratefully acknowledged.

REFERENCES

(1) a. E. Vogel, W. Grimme and E. Dinné, Angew. Chemie 75, 1103 (1963).

b. K. G. Untch and D. J. Martin, Private communication to E. Vogel.

(2) L. Skatteböl, Tetrahedron Letters 1961, 167.

(3) This same rearrangement has been independently observed by L. Skatteböl (private communication to E. Vogel).

(4) Other rearrangements of 10-membered ring hydrocarbons containing the 1,5-hexadiene system include the rearrangement of 1,5-cyclodecadiene to 1,2-divinylcyclohexane [C. A. Grob, H. Link and P. W. Schiess, Helv. Chim. Acta 46, 483 (1963); G. Wilke, Angew. Chemie 75, 10 (1963)], and 1,3,5,8-cyclodecatetraene, which gives 1,4,9,10-tetrahydronaphthalene [C. A. Grob and P. W. Schiess, Helv. Chim. Acta 47, 558 (1964)].

(5) For recent reviews of the Cope rearrangement, see E. Vogel, Angew. Chemie internat. Edit. 2, 1 (1963), and S. J. Rhoads, in Molecular Rearrangements, Part 1, edited by P. de Mayo, p. 655, Interscience Publishers, New York, 1963.