

THERMAL BEHAVIOR OF TRANS,TRANS,TRANS-1,2,3,4-TETRAVINYL-CYCLOBUTANE

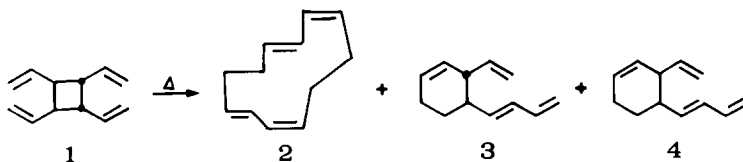
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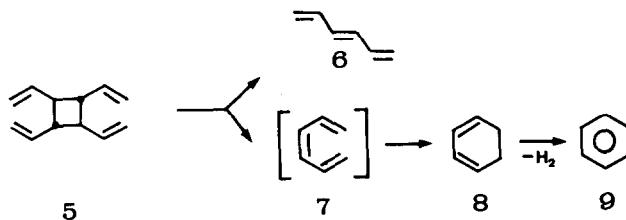
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Above 420°C the title compound decomposes to *trans*-hexatriene and cyclohexadiene-1,3. At temperatures above 770°C only cyclohexadiene-1,3 and benzene are found.

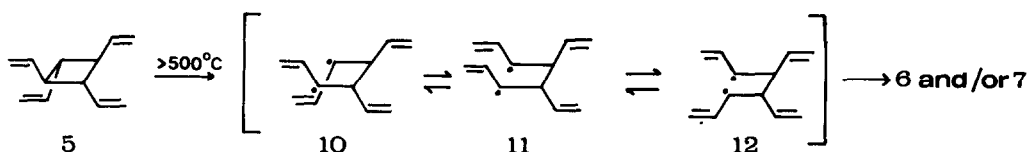
Cis,trans,cis-1,2,3,4-tetravinylcyclobutane (1) rearranges above 120°C in 1,3,7,9-cyclododecatetraene (2) and *anti* and *syn* 4-butadienyl-3-vinyl-1-cyclohexene (3 and 4)¹. This reaction can be rationalized by assuming a Cope rearrangement between the *cis*-divinyl groups via a boat-like transition state. For *trans,trans,trans*-1,2,3,4-tetravinylcyclobutane (5)² a boat-like transition state is not possible and a chair like is much less favoured for steric



reasons³. To study its thermal behavior we have heated 5 in the gas phase between 200 and 800°C in a quartz tube under reduced pressure (10^{-1} - 10^{-3} Torr). In contrast to 1, 5 is thermally stable up to 420°C in the gas phase. Around 530°C an almost quantitative decomposition into *trans*-hexatriene (6) and cyclohexadiene-1,3 (8) has been found in the approximate ratio of 1:1. With increasing temperature the ratio 6:8 decreases so that at 770°C no 6 can be detected any more, instead benzene (9) is found in an increasing amount. The occurrence of 8 and 9 can be understood by assuming *cis*-hexatriene (7) as an intermediate.



The different behavior of 5 compared to 1 can be rationalized by assuming a breaking of one cyclobutane C-C bond. The biradical intermediate (10) either further decomposes to 6 or isomerizes to 11 or 12. The latter decompose to 6 and/or 7 respectively as indicated below. From the fact that no C_{12} hydrocarbons like 2-4 or 1,2,3-trivinylcyclohexene-4 could be detected we infer



that at temperatures above $400^\circ C$ and at reduced pressure the decomposition of 10-12 is favoured compared to any further rearrangement. In line with our interpretation are experiments by Vogel³ as well as Hammond and De Boer⁴ which show that *trans*-1,2-divinylcyclobutane (13) rearranges thermally via a biradical intermediate. Furthermore it is reported that during the thermolysis of 13⁴ and of 8⁵ the amount of butadiene or benzene, respectively, increases with increasing temperature.

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References

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