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THERMAL REARRANGEMENTS OF CYCLIC ALLENES *via* RETRO-ENE REACTIONS

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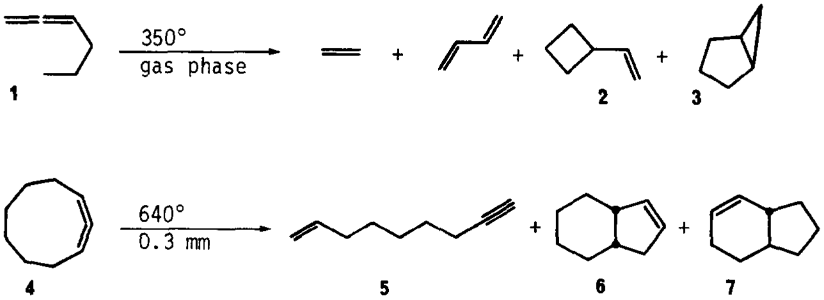
ABSTRACT: Flow vacuum thermolysis (500-650°) of 1,2-cyclonona- and 1,2-cyclodecadienes yields, as primary products, terminal enynes and enedienes. Secondary intramolecular Diels-Alder reactions of the enedienes afford *cis* and *trans* bicyclics.

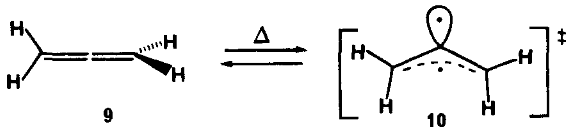
During the course of studies on allene photochemistry,[1,2] we have found it desirable to carefully examine the high temperature thermal reactions of homologous allenes, 1,2-cyclononadiene and 1,2-cyclodecadiene. We report here facile ring fragmentation, which results from two distinct modes of intramolecular hydrogen transfer.

Previous studies of unimolecular allene thermal chemistry[3] have concerned principally the rotational barrier,[4] Cope rearrangements,[5] interconversion with propynes and cyclopropenes,[3c,6] sigmatropic shifts in vinylallenes,[7] and more complex rearrangements.[3a,b] Among simple alkyl substituted allenes, Ward and Karafiath reported[8] that pyrolysis of 1,2-hexadiene (**1**) gives [Scheme I] ethylene, butadiene, and cyclization products **2** and **3**. The same products were observed in photochemical reactions. Crandall and Watkins have described thermal rearrangement of 1,2-cyclononadiene (**4**) to enyne **5** and bicyclics **6** and **7**.[9] The authors speculated that intramolecular hydrogen abstraction by biradical **8** provides a route to products. More recently, it has been recognized that the analogous bent (*ca*. 130°) biradical **10** should correspond to the allene thermal rotational barrier.[10] This is a potential surface

Scheme I



8

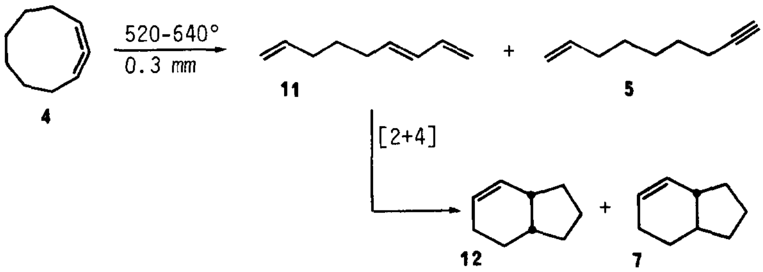


9 **10**

saddle point or transition state,[10c] rather than an intermediate.

Flow vacuum thermolysis of allene **4** at 640° yielded three isomers, as described earlier.[9] However, we assign the structure of one of the bicyclics [Scheme II] as **12**, rather than **6**,[11] based upon independent synthesis from a known ketone precursor.[2] Thermolysis of **4** at progressively lower temperatures permitted observation of increasing amounts of a fourth isomer; this was isolated by preparative GLC and characterized (MS, ^{1}H NMR, retention time) as pure trans-enediene **11**.[12] Product ratios from GLC analyses[13] are collected in Table I.

Scheme II



In like manner, thermolysis of 1,2-cyclodecadiene [Scheme III, Table I] afforded enyne **15**,[14] cis and trans bicyclics **16** and **17**, and enediene **14**. Thermolysis of GLC purified **14** yielded **16** and **17** in the same ratio as from **13**. Several unidentified minor products also were observed; their structures are under investigation.

Scheme III

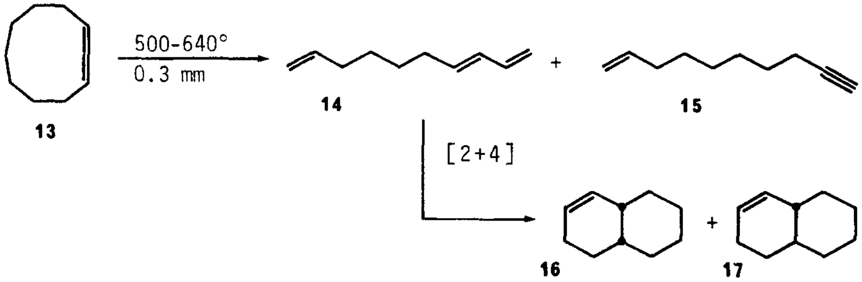
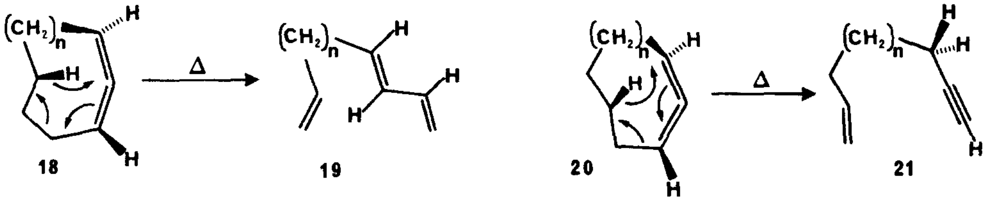


Table I. Product Distributions From Flow Thermolyses.

Substrate	Temperatures	Products (% of total)					
		4	11	5	12	7	total other products
4	640°	3.9	0	39.6	38.2	16.2	3.1
4	580°	64.8	2.1	20.0	7.7	5.4	0
4	520°	91.4	1.1	1.1	3.0	2.1	1.3
5	640°	0	0	90	0	0	10
		13	14	15	16	17	total other products
13	640°	0	1	5	31	34	29
13	580°	11	9	4	29	31	16
13	520°	59	11	2	10	11	7
13	500°	91	4	0.4	1.2	1.4	2.0
14	640°	0	0	0	40	42	28

These results demonstrate that enedienes **11** and **14** are primary thermal products and further imply that bicyclic structures result from well-precedented intramolecular Diels-Alder cyclizations.[15] Isomers **5** and **11** also are among the vapor phase photochemical products of 4.[2] There are thus two ring fragmentation modes in cyclic allenes, one leading to enynes,[9] the other to enedienes. Both modes may be described as symmetry allowed $[\sigma 2 + \sigma 2 + \pi 2]$ six electron processes, (*i.e.*, "retro-ene" reactions[16]). As noted earlier,[9] this requires substantial deformation from a linear allene. Theoretical studies demonstrate that ground state π bond rotation and C_1-C_2-C_3 bending are coupled motions in allene.[10c] Thus, we envision effectively concerted rearrangement from a geometry (**18** or **20**) in which the allene is strongly bent, but not yet planar. A stepwise diradical process may obtain in less constrained acyclic systems.[8] Similar "retro-ene"-type fragmentations have been reported for cyclooctene[17a] and cyclononene.[17b]



18 **19** **20** **21**

In concluding, we note that mass spectral studies by Djerassi and co-workers show remarkably similar fragmentations (McLafferty rearrangements) in allene radical cations.[18]

We are continuing to explore the generality and mechanism of these processes.

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