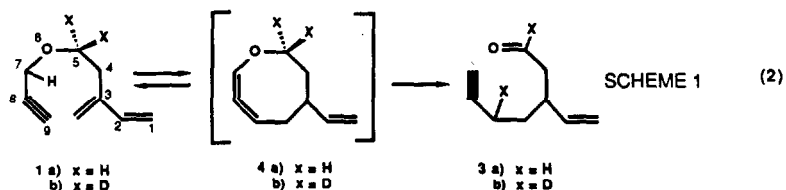
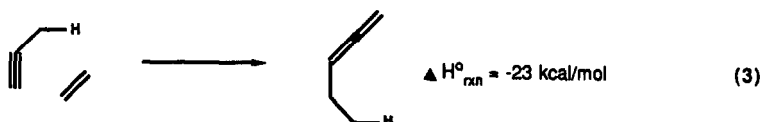


tinguished by the absence of the triplet at 9.72 ppm and the appearance of a single proton multiplet at 2.16 ppm. The oxacycloallene **4** apparently does not accumulate under the reaction conditions since an effort to detect this compound in the crude thermolysis mixture was not successful.



The first step in the rearrangement involves generation of a relatively strained 1,2-cyclooctadiene ring. This carbocycle has a calculated strain energy of approximately 14 kcal/mol.⁹ The feasibility of cyclization may be evaluated by consideration of the energetics of the parent ene reaction (eq. 3), estimated using group equivalents¹⁰ to be exothermic by 23 kcal/mol. The net enthalpy change for the first step in equation 2, therefore, may be roughly estimated to be exothermic by 9 kcal/mol.¹¹



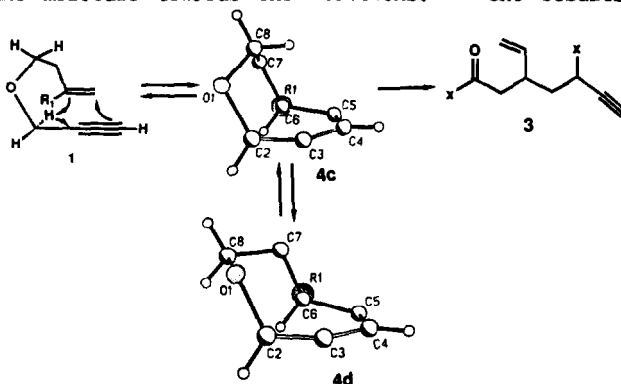
The second step in the rearrangement, a retro-hetero ene fragmentation¹² of a cycloallene, is well precedented. Earlier work by Crandall¹³ and more recent work by Johnson¹⁴ report that the FVT of 1,2-cyclononadiene yields, among other products, 1,8-nonyne, a product directly analogous to aldehyde **3**.

The failure to detect cycloallene as a thermolysis product suggests a facile fragmentation reaction.¹¹ 1,2-cyclooctadienes are calculated to have several low energy conformations.⁹ From consideration of the stereoelectronic requirements for the concerted ene cyclization, the most plausible transition state leads to twist-boat conformation (4c) of cyclic oxallene **4**. In this conformation the syn-hydrogen at C-8 is suitably disposed for delivery to the allenic carbon at C-4. Other conformations of the cycloallene (i.e., twist chair 4d), which are estimated to be separated by a barrier in excess of 8 kcal/mol,⁹ do not permit hydrogen transfer from C-8.

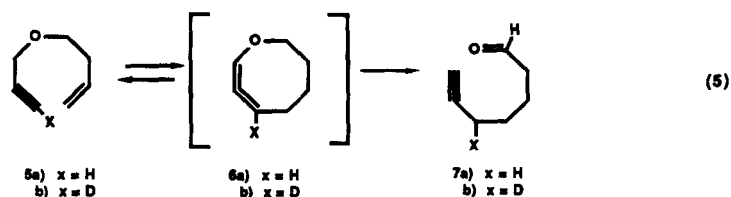
Johnson has recently shown that nine and ten membered cyclic allenes have several fragmentation manifolds available that could, in the case of cyclooxallene **4**, result in the formation of isomeric oxadiene fragmentation products. Although we cannot at this point rigorously rule out some contribution from this pathway, these regioisomeric fragmentations must be relatively unimportant. The high regioselectivity for fragmentation of cyclic oxallenes **4** may result from the activating influence of the oxygen heteroatom, and the aforementioned conformational bias.

In an effort to develop an understanding of the structural requirements for the rearrangement, enyne ether **5** was subjected to the thermolysis conditions. At temperatures in excess of 480°C, aldehyde **7** was found to be a product of the thermolysis mixture. The yield of aldehyde **7** was only 3-5% based upon enyne ether **5**. The dominant reaction manifold at these temperatures

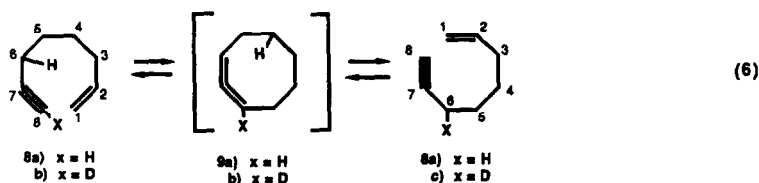
involves a characteristic ene fragmentation to produce 1,2-propadiene and 4-pentyn-1-ol.^{1,2} The harsher conditions required for the reaction of 5 compared with 1 implies the vinyl substituent at C-3 activates the molecule towards ene reactions.¹⁵ The results of deuterium labeling



studies employing substrate (5b) were consistent with the proposed two-step reaction involving transient formation of the cyclic oxallene intermediate 6.



A deuterium labeling study has revealed that the parent hydrocarbon, 1,7-octenyne (8), also undergoes a similar reaction. Upon exposure of enyne 8b at atmospheric pressure to temperatures of 490°C (contact time 10 sec), 50% scrambling of deuterium between positions C-8 and C-6 was observed (eq. 5). It is important to note that 1-²H-1-decyne does not exhibit scrambling under these same reaction conditions. Although 1,2-cyclooctadiene (9) has not been isolated from this reaction, its generation by an intramolecular ene cyclization is strongly implied.



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11. (a) Group equivalents for calculating ⁰S are not available. By comparison with related cyclizations to form eight-membered rings,^{11b} the entropy of the ene cyclization may be estimated to be approximately -20 eu. This would imply that at the high temperatures necessary for these cyclizations, the equilibrium concentration of oxallene 4 would be quite low. (b) Shea, K.J.; Burke, L.D.; England, W.P. J. Am. Chem. Soc. 1988, 110, 0000.
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14. Price, J.D.; Johnson, R.P. Tetrahedron Lett. 1985, 26, 2499.
15. Aldehyde 7a ¹H NMR (250 MHz, CDCl₃) δ 9.77 (t, J=1.6 Hz, 1H), 2.47 (t,d J=7.1, 1.7 Hz, 2H), 2.22 (t,d J=6.9, 2.6 Hz, 2H), 1.96 (t J=2.6 Hz, 1H), 1.76 (m, 2H), 1.56 (m, 2H). ¹³C NMR (62.9 MHz, CDCl₃) δ 202.2, 83.9, 68.9, 43.4, 28.0, 21.3, 18.3. Mass spectrum m/e (70 eV, isobutane, rel %) 113(3), 112(8), 111(100), 110(5), 109(15), 95(11), 93(86), 83(90). Aldehyde 7b ¹H NMR (250 MHz, C₆D₆) δ 9.29 (s, 1H), 1.85 (m, 2H), 1.74 (t J=6.7 Hz, 2H), 1.4 (m, 2H), 1.2 (m, 2H). Mass spectrum m/e (CI, isobutane- GCMS, rel %) 113(10), 112(100), 111(9), 110(16), 109(3), 98(9), 94(33), 93(19), 84(83), 83(27).
16. For a related finding see Snider, B. Acc. Chem. Res. 1980, 13, 426.
17. Figures 4c and 4d were generated using known coordinants for the twist boat and twist chair conformations of 1,2-cyclooctadiene.⁹ Hydrogens were added using standard crystallography programs with bond distances of 0.95 Å. Distances between H(8_{yn}) and C(4) for twist boat 4c and twist chair 4d are 2.64 and 4.58 Å, respectively.

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