

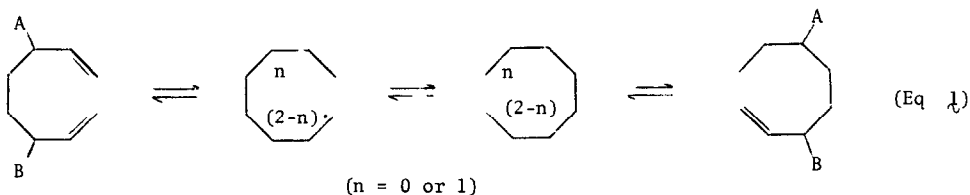
PYROLYSIS OF ALLYL 3-BUTENYL ETHERS A FORMAL [4,4] SIGMATROPIC SHIFT

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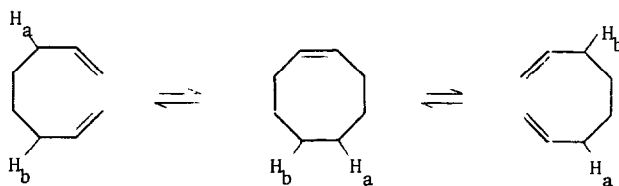
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In theory a [4,4] sigmatropic shift¹ could occur, but it would require the intermediacy of a biradical ($n = 1$ in equation 1) or zwitterion substrate ($n = 0$ in equation 1). Structurally the [4,4] shift would necessitate two additional positional changes symbolized by A and B (equation 1). Thus one intuitively suspects that the true [4,4] sigmatropic shift will prove to be

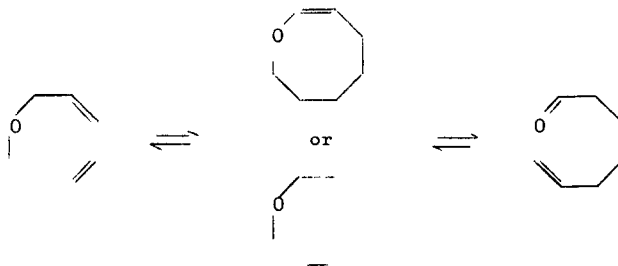


an unlikely event². Implicit in the literature of the ene reaction³ for some years has been the possibility of achieving a *formal* [4,4] shift, i.e. the same overall structural result. For example the well-known equilibrium between 1,7-octadiene and cyclo-octene clearly permits a *formal* [4,4] shift via an ene reaction followed by a retro-ene process. This could be readily demonstrated via the use of a properly labeled molecule. As far as we are aware, this dormant

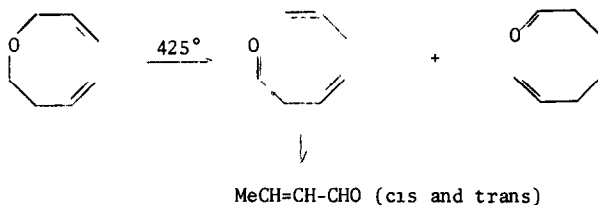


rearrangement has not been previously stirred into reality

An alternative route to rendering this degenerate [4,4] shift reaction visible, which has also the advantage of rendering it essentially irreversible, is to use an ether which will be converted to a carbonyl product. Allyl butenyl ethers are of this type and are readily available synthetically which could make the overall process attractive preparatively. We have

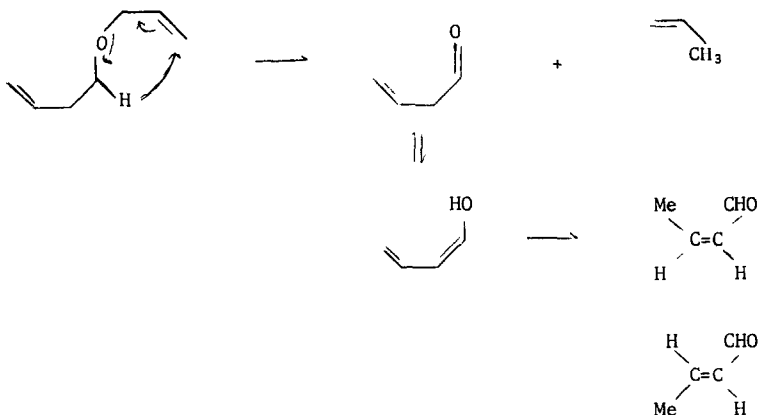


pyrolyzed allyl 3-butenyl ether in a flow system at 400-450° using nitrogen as a carrier gas. Below 400° no reaction was observed, while between 400-425° at contact times of 30-60 sec, three condensable products appear. Longer times or higher temperatures led to large amounts of non-

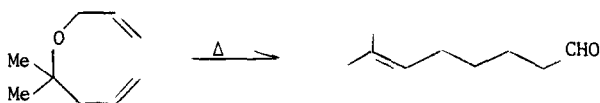


condensable material. The main product, vinylacetaldehyde and its hydrogen shift isomers *cis*- and *trans*-crotonaldehyde, is derived from a retro-ene reaction,⁵ but a modest amount (between 5 and 15% of the condensable material) of 6-heptenal is obtained. Synthesis of an authentic sample from 1,7-octadiene, via monoepoxidation, hydrolysis and periodate cleavage confirmed the identity of the latter product.

We assume that the retro-ene reaction to give vinylacetaldehyde is followed by enol formation and a 1,5-hydrogen shift to give *cis*-crotonaldehyde (about 75% of mixture of isomers) followed by a thermal *cis*-*trans* isomerization. Blocking the retro-ene reaction leads to the [4,4]



shift becoming the main reaction Thus at 450-500° pyrolysis of allyl 1,1-dimethyl-3-butenyl

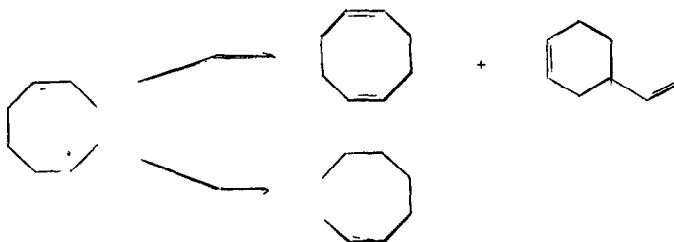


ether gives isolable yields of 7-methyl-6-octenal up to 35% Further study of this interesting use of the ene reaction is in progress

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References

- 1 R B Woodward and R Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH Weinheim, Germany, 1970, p 114
- 2 The [4,4] sigmatropic shift must compete with direct ring closure processes (below)



Since the [4,4] shift must break a bond it should require a large activation energy compared to the small activation energy for the ring closure

- 3 a) H M R Hoffmann, *Angew. Chem. Internl Edit. Engl.*, **8**, 556 (1969),
b) W R Roth, *Chimia*, **20**, 229 (1966)
- 4 See ref 2b, p 230
- 5 R C Cookson and S R Wallis, *J. Chem. Soc. (B)*, 1245 (1966)