Stereochemical Requirements of Acetylenic Retro-ene Transition States†

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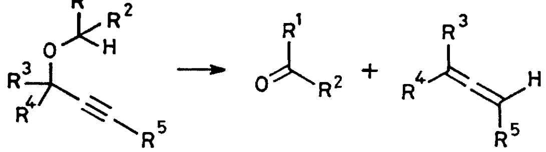
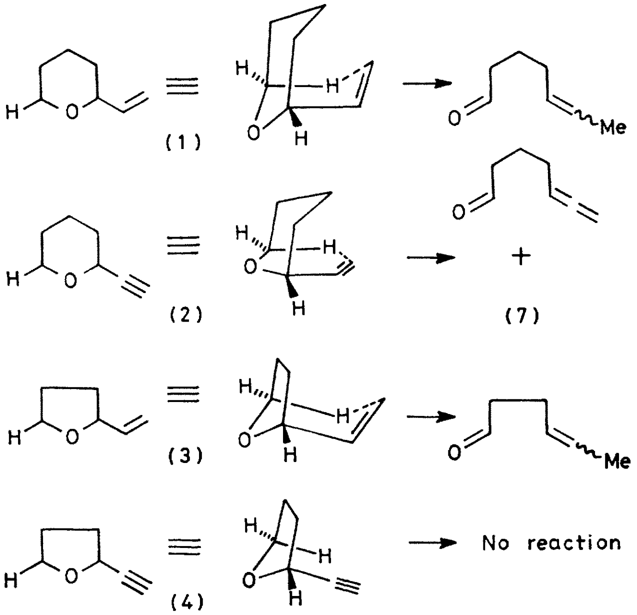
Summary Retro-ene reactions of acetylenic and olefinic substrates differ in the stereochemical requirements of their respective transition states; reactions of olefins proceed *via* a chair-like (or boat-like) configuration while those of acetylenes require planarity.

Although it is generally assumed that ene and retro-ene reactions of olefinic substrates proceed *via* a chair-like (or boat-like) transition state geometry,[1] the requirement for the corresponding acetylenic substrates remains in doubt. After consideration of the minimal distortion of the normal sp bond angle of 180° for acetylenes, the spherical symmetry of acetylenic π systems, and the relative magnitudes of alkyl substituent effects, we have previously suggested[2] that the transition state for the retro-ene reaction of β-hydroxyacetylenes requires a planar array of all six participating atoms with resulting maximum overlap of all reacting orbitals in the cyclic array. The resulting orbital interactions permit a high degree of 'aromaticity' in the transition state which may in part account for the observation that acetylenes have invariably reacted at faster rates than their olefinic analogues in which such good orbital interactions are not possible. This suggestion has been challenged[3] on the bases of a maximum kinetic isotope effect as well as other substituent effects. We now report unequivocal proof that the ability of an acetylenic substrate to assume a planar configuration is essential in order for the retro-ene reaction to occur.



The retro-ene reaction of alkyl prop-2-ynyl ethers has been reported[4,5] to yield the expected allene and carbonyl fragmentation products. The olefinic ethers (**1**) and (**3**) were prepared by modifications of the published procedures,[6] as were their acetylenic analogues (**2**) and (**4**).[7] Molecular models show that the two olefinic ethers can readily assume the indicated chair-like conformations normally preferred for their retro-ene fragmentation. Both compounds readily decomposed upon flow system,[8] vapour-phase thermolysis at 450—470 °C to give the expected products at rates commensurate[4] with the degree of alkyl substitution upon the corresponding acyclic reacting system.


(1)

(2)

(7)

(3)

(4)

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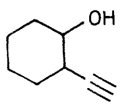
† For paper No. 7 in the series Intramolecular Pericyclic Reactions of Acetylenes, see reference 5.

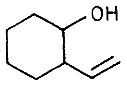
By contrast, the behaviour of the acetylenic substrates (**2**) and (**4**) differs substantially from that of their acyclic analogues Models clearly indicate that (**2**) can assume a planar conformation for the six reacting atoms only at the cost of considerable angle strain within the confining tetrahydropyran structure A consequence of this strain is that (**2**) represents the first substrate in our studies in which the acetylenic analogue does not react faster than the corresponding olefinic compound Furthermore, the retro-ene fragmentation of (**2**) is accompanied by the indicated cyclization reaction[9] which has not been observed in any acyclic substrates and which can apparently compete with the retro-ene process only when the latter is hindered

Models indicate that compound (**4**) can attain the requisite planar array only at the cost of a prior bond rupture owing to the constraints enforced by the 5-membered tetrahydrofuran ring Compound (**4**) proved to be essentially thermally stable at 470 °C with $> 99\%$ recovery under conditions where its olefinic analogue (**3**) had almost completely reacted

It appears clear, therefore, that the retro-ene reaction of acetylenic substrates is inhibited when structural requirements restrict planarity of the reacting 6-atom system It is this factor which is undoubtedly responsible for the report[10] that (**5**) does not react in the β-hydroxyolefin cleavage whereas its olefinic analogue (**6**) does However, both (**5**) and (**6**) were prepared by the addition of appropriate organometallic reagents to cyclohexene oxide, so that the resulting *trans*-geometry can readily accommodate a chair-like transition state for (**6**) while no planar arrangement is possible for (**5**)



(5)



(6)

(7)

It is obvious that olefinic and acetylenic substrates differ considerably in the geometric requirements of their respective transition states, previous claims[3] notwithstanding This factor must be considered as such reactions are increasingly utilized for synthetic purposes [11]

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[8] The apparatus has been described previously A Viola, E J Iorio, K K Chen, G M Glover, U Nayak, and P J Kocienski, *J Am Chem Soc* , 1967, **89**, 3462

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[11] For a review see W Oppolzer and V Snieckus, *Angew Chem* , *Int Ed Engl* , 1978, **17**, 476