# Homoallyl Ether Rearrangement. A Reaction Proceeding *via* a Cyclic Eight-centred Transition State

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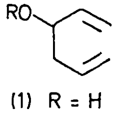
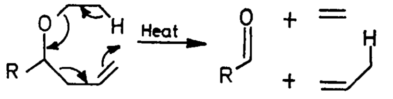
*Summary* The thermolysis of homoallyl ethers proceeds in a concerted manner *via* an eight-centred transition state; thermolysis of 1-ethoxy-1-phenylbut-3-ene at 330—400° follows a first-order rate law, with $E_a = 43$ kcal/mol, $\Delta S^\ddagger = -10$ cal $K^{-1}$ $mol^{-1}$, affording ethylene, benzaldehyde, and propene as the only products, and the corresponding butyne derivative behaves similarly, giving allene as the only three-carbon fragment.

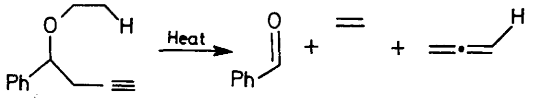
A LARGE number of organic reactions are known to proceed *via* cyclic six-membered transition states, but only a few authenticated examples proceed *via* larger cyclic transition states,[1] and essentially all of these concern [1,7] sigmatropic hydrogen migrations through a conjugated system.† The concerted rearrangement of homoallyl‡ ethers reported herein represents the first example of a concerted fragmentation involving a [1,7] hydrogen transfer with only a terminal olefinic receptor site across an otherwise σ bonded system.



(1) R = H
(2) R = Et



(2) R = vinyl
(3) R = Ph
(4) R = H



(5)

As part of our continuing interest in the oxy-Cope system (**1**),[2] 3-ethoxyhexa-1,5-diene (**2**) was thermolysed in the previously described vapour-phase flow system.[3] In addition to the expected products, acrolein was detected, which can only be formed from the first three carbon atoms of (**2**) and its ethereal oxygen. A pericyclic reaction, involving an eight-centred transition state leading to acrolein, ethylene, and propene can then be envisaged.

Since the three known six-centred pericyclic processes possible in (**2**) require the initial presence of the vinyl group [*i.e.*, C(1)–C(2)] the thermolysis of (**3**) was investigated, where this vinyl group is replaced by a phenyl substitutent. Since we are unaware of any phenyl participation in un-

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† The numerous reported examples of [1,7] sigmatropic hydrogen transfers in cycloheptatrienyl systems may be sequential [1,5] migrations (K. W. Egger, *J. Amer. Chem. Soc.*, 1967, **89**, 3688). An example of a sigmatropic shift of still higher order involves a degenerate [1,9] shift across a conjugated fused ring system (C. W. Rees and K. P. Parry, *Chem. Comm.*, 1971, 833).

‡ The term 'homoallyl' is used to emphasize the similarity of this reaction to the allyl and vinyl ether rearrangements.

catalysed Cope reactions[§] or of non-radical benzyl ether decomposition, (**3**) should provide an ideal testing ground for the proposed eight-centred process, particularly since the bond dissociation energy of the breaking benzylic bond is 2 kcal/mol lower than that of the corresponding allylic bond.[4]

Compound (**3**) was prepared from 1-phenylbut-3-en-1-ol, NaH, and EtBr, in benzene solution, in 60% yield (b.p.[5] 65° at 2 mmHg). Thermolysis of (**3**) at 400° under nitrogen gave only benzaldehyde (42% conversion), ethylene, propene, and starting material.

The gas-phase kinetics of (**3**) were followed in the apparatus previously described.[6] The reaction obeyed the first-order rate equation for several half-lives; $k \times 10^4/\text{s}^{-1} =$ 6·62(360°), 3·72(350°), 2·15(340°), and 1·18(330°). The resulting linear Arrhenius plot (correlation coefficient = 0·9999) affords[¶] $E_a = 43{\cdot}4$ kcal/mol, $\log A = 11{\cdot}3$, and $\Delta S^{\ddagger} = -10$ cal K$^{-1}$ mol$^{-1}$. The reaction rate constant was unaffected by a five-fold increase in surface area, by variations in initial concentrations by a factor of five, or by changing the reaction tubes used from Pyrex to soft glass.

The above facts suggest that the fragmentation of the homoallyl ether (**3**) is a homogeneous, first-order, unimolecular process. Both the low activation energy, which implies energetic assistance in the bond-breaking step, and the negative entropy of activation, indicative of a rigid transition state, implicate a concerted process.

The 'inversion' of the three-carbon fragment in (**3**), with migration of the double bond, was verified by the thermolysis of the acetylenic analogue (**5**).[**] The similarities between reactions involving acetylenic and olefinic bonds in intramolecular cyclic six-centre transition states have been well established.[7] Thermolysis of (**5**) in the range 330—360° proceeded in a manner analogous to that of (**3**), with $E_a = 40{\cdot}9$ kcal/mol and $\Delta S^{\ddagger} = -14$ cal K$^{-1}$ mol$^{-1}$.

No propyne absorption was detectable in the n.m.r. spectrum of the thermolysate which did, however, show a strong singlet at $\delta$ 4·67 (allene). Thus, the thermolysis of (**5**) provides further evidence for the participation of an eight-centred transition state.

A phenyl substituent on a breaking bond generally decreases the activation energy of pericyclic processes by *ca.* 4 kcal/mol. Therefore, the expected activation energy for the unperturbed concerted homoallyl ether rearrangement of (**4**), *ca.* 47 kcal/mol, is only 2—3 kcal/mol higher than that of the analogous six-centred process in ethyl vinyl ether.[8] Consequently, eight-centred processes should be readily attainable, particularly in systems where analogous six-centred processes are blocked.

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[§] The 'C-Claisen rearrangement' requires the presence of a base catalyst (W. von E. Doering and R. A. Bragoli, *Tetrahedron*, 1966, **22**, 385).

[¶] These parameters are corrected for the statistical effect due to three equivalent transferrable hydrogen atoms. The expected accuracy of $E_a$ is $\pm 1{\cdot}5$ kcal/mol and that of $\Delta S^{\ddagger}$ is $\pm 2$ cal K$^{-1}$ mol$^{-1}$. The entropy of activation is calculated from the expression $A = e(K/h)T_m \exp \Delta S^{\ddagger}/R$.

[**] Compounds (**3**) and (**5**) afforded n.m.r. and i.r. spectra as well as combustion analyses consistent with the desired structures.

[1] J. L. A. Schlatman, J. Pot, and E. Havinga, *Rec. trav. Chim.*, 1964, **83**, 1173; M. Akhtar and C. J. Gibbons, *Tetrahedron Letters*, 1965, 509; L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, 1968, **90**, 1540; R. Hug, H.-J. Hansen, and H. Schmid, *Chimia*, 1969, **23**, 108.
[2] A. Viola, J. H. MacMillan, and R. J. Proverb, *Chem. Comm.*, 1971, 936 and references cited therein.
[3] A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *J. Amer. Chem. Soc.*, 1967, **89**, 3462.
[4] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, Table A.22, p. 215.
[5] G. K. Abdullaev, *Uch. Zap. Azerb. Gos. Univ.*, 1956, **1**, 23 (*Chem. Abs.* 1958, **52**, 5328b).
[6] A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, 1971, **93**, 6967; Method A.
[7] A. Viola, J. H. McMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, 1971, **93**, 6967; A. Viola, R. J. Proverb, B. L. Yates, and J. Larrahondo, *ibid.*, 1973, **95**, 3609; H. Kwart, S. F. Sarner, and J. Slutsky, *ibid.*, 1973, **95**, 5234, 5242.
[8] S.-N. Wang and C. A. Winkler, *Canad. J. Res.*, 1943, **21B**, 97; A. T. Blades and G. W. Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1039.