Tetrahedron Letters No. 36, pp 3121 - 3124, 1975. Pergamon Press. Printed in Great Britain.

THE THREE MECHANISMS FOR COPE REARRANGEMENT OF 1,5-HEXADIENE

Donald C. Wigfield and Kevser Taymaz
Department of Chemistry, Carleton University
Ottawa, Canada

(Received in USA 25 June 1975; received in UK for publication 24 July 1975)

There is evidence that Cope Rearrangements may occur by as many as four distinct mechanisms, of which only one is the usual concerted mechanism (1). In 1972, Goldstein and Benzon reported the discovery of a second degenerate rearrangement of 1,5-hexadiene, occurring only at high temperature (250-300°), experimentally distinct from the normal concerted mechanism by virtue of loss of stereointegrity from 1,5-hexadiene-1,3,4,6-d_4 (2). If, as the authors suggest, this high temperature rearrangement is concerted, it represents yet another mechanistic variety in the Cope Rearrangement - a second concerted mechanism. The evidence presented, however, seemed to us not to completely exclude the possibility that the new high temperature rearrangement might be a further example of the radical dissociation-recombination mechanism which clearly would also be consistent with the observed racemization and with the observed near zero value of $\Delta S^{\neq}$ (-3.0 ± 3.6 e.u.) (3). In particular, the activation parameters reported ($\Delta H^{\neq}$ = 44.7 kcals/mole; $\Delta S^{\neq}$ = -3.0 e.u.), while quite different from enthalpy and entropy differences between 1,5-hexadiene and two allyl radicals (ΔH = 62 kcals/mole; ΔS = +35 e.u.), combine to give a value of free energy ($\Delta G^{\neq}$ = 46.3 kcals/mole) similar to that calculated from the equilibrium data (ΔG = 44 kcals/mole) (4). Thus, in the absence of a barrier to radical recombination it would appear that at 250° both the new rearrangement and dissociation-recombination would take place at comparable rates. Even taking into account the value of the free energy barrier to radical recombination, which can be estimated from the data of Benson and co-workers (5) as approximately 5 kcals/mole, the value of $\Delta G^{\neq}$ for dissociation (49 kcal/mole) is still within experimental error with the $\Delta G^{\neq}$

observed for the new high temperature rearrangement. The discrepancy between the values of the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ components of the free energy barriers is reduced by consideration of the data of Benson et al (5) which shows that the rate of recombination of allyl radicals decreases with increasing temperature; thus this recombination would appear to be one of those rare (6) cases of a reaction having a transition state barrier due entirely to entropy, with a <u>negative</u> enthalpy of activation. Using these data, the barrier appears to be composed of $\Delta H^{\neq}_{recomb}$ = -7 kcals/mole, and $\Delta S^{\neq}_{recomb}$ = -23 e.u. Thus the activation parameters for the dissociation reaction will differ considerably from the equilibrium values, $\Delta H^{\neq}_{dissoc}$ = 62-7 = 55 kcals/mole, and $\Delta S^{\neq}$ = 35-23 = 12 e.u., values that, while closer, still differ from those reported by Goldstein and Benzon for the new rearrangement by about 10 kcals/mole in $\Delta H^{\neq}$ and 15. e.u. in $\Delta S^{\neq}$.

Subsequent to 1972, experimentation has been in progress both at Carleton and Cornell to confirm or deny distinction between the new high temperature rearrangement and the dissociation-recombination mechanism. In both cases this has centred on crossover experiments, and the Cornell work, showing the lack of crossover products from 1,6- and 3,4-dideuterated 1,5-hexadienes at 282^{o} has already been published (7). This communication reports our own studies on unlabelled and 1,1,6,6-tetradeuterio-1,5-hexadiene, and on 2-methyl-1,5-hexadiene which specify more precisely the temperatures required for the various mechanisms to occur.

1,5-Hexadiene-1,1,6,6-d_4 was prepared from adipic acid by the route of Sunko et al (8). This was mixed with an excess of unlabelled 1,5-hexadiene, and the mixture repeatedly passed through a U-tube at various temperatures <u>in vacuo</u>. The product mixture was then analyzed by mass spectrometry to determine whether the crossover product, 1,5-hexadiene-1,1-d_2 (M.W. 84) had been formed. It was found that the threshold temperature for detection of crossover is approximately 360^{o}. Beyond that temperature, (e.g. 395^{o}), the presence of the M/e 84 peak (9) became progressively larger; it should be mentioned, however, that this crossover reaction also coincided with the reaction mixture no longer remaining completely clean, as judged by spectral examination of the product. Representative results are shown in the Table (10).

Mixture of d_0 and d_4 1,5-hexadienes	Mass spectral relative intensities[(a)]		
	M/e 86	M/e 85	M/e 84[(b)]
Unheated	1.0	2.7	2.4
Passed through tube 24 times at 350°[(c)]	1.0	2.9	2.0
Passed through tube 17 times at 395°[(c)]	1.0	2.1	12.0

(a) Relative to M/e 86. (b) M/e 81, 82 very large; M/e 83 ambiguous due to contribution from M/e 82. (c) Material took <1 sec. to pass through tube, but no attempt to obtain accurate contact times was made.

While the above results are clearly consistent with the formation of 1,5-hexadiene-d_2 by a dissociation-recombination mechanism at 395°, because of the difficulties of analysis due to the mass spectral fragmentation ($M^{\oplus}$-H, $M^{\oplus}$-D), and the ambiguities of decomposition, similar pyrolyses were also carried out on 2-methyl-1,5-hexadiene. As expected, no 1,5-hexadiene or 2,5-dimethyl-1,5-hexadiene were detectable until the temperature reached 360 - 390°, at which point small amounts of these cross products were formed. At 460° considerable crossover occurred (10%), consistent with the report of Huntsman (11).

From these results a more complete picture of the mechanisms of Cope Rearrangement of 1,5-hexadiene emerges. At temperatures below 240° rearrangement is purely the "low temperature" concerted mechanism, joined at 259-295° (2) by the "high temperature" concerted mechanism, and finally at 360-390° by the dissociation-recombination mechanism. The conclusion of Goldstein that at 300° rearrangement is purely concerted (2, 7), despite the thermochemical argument, is confirmed.

Acknowledgments

We acknowledge a stimulating correspondence with Professor Goldstein, and exchange of experimental results, eventually leading to total agreement regarding the relative importance of these mechanisms under various conditions. This work was funded by the National Research Council of Canada.

References and Notes

1. For a discussion of the mechanism multiplicity, see D.C. Wigfield, S. Feiner, G. Malbacho, and K. Taymaz, Tetrahedron, 30, 2949 (1974).
2. M.J. Goldstein and M.S. Benzon, J. Amer. Chem. Soc., 94, 7147 (1972).
3. G.S. Hammond and C.D. DeBoer, J. Amer. Chem. Soc., 86, 899 (1964).
4. All thermodynamic values refer to 250°.
5. D.M. Golden, N.A. Gac, and S.W. Benson, J. Amer. Chem. Soc., 91, 2136 (1969).
6. K.J. Laidler, Theories of Chemical Reaction Rates. McGraw-Hill Book Company, New York 1969. pp. 76-79.
7. M.J. Goldstein and M. DeCamp, J. Amer. Chem. Soc., 96, 7356 (1974).
8. K. Humski, R. Malojcic, S. Borcic, and D.E. Sunko, J. Amer. Chem. Soc., 92, 6534 (1970).
9. The possible origin of the M/e 84 peak by loss of deuterium (e.g. by wall exchange) appears unlikely on the basis of nmr analysis of the product, showing an overall loss of <5% of deuterium.
10. Similar crossover products from 1,5-hexadiene-1,1-d_2 have previously been observed at 383°. W. von E. Doering, V.G. Toscano and G.H. Beasley, Tetrahedron, 27, 5299 (1971).
11. W.D. Huntsman, J. Amer. Chem. Soc., 82, 6389 (1960).