

REACTIONS AT HIGH PRESSURE, PART 10: THE VOLUME PROFILE OF AN INTRAMOLECULAR
DIELS-ALDER REACTION

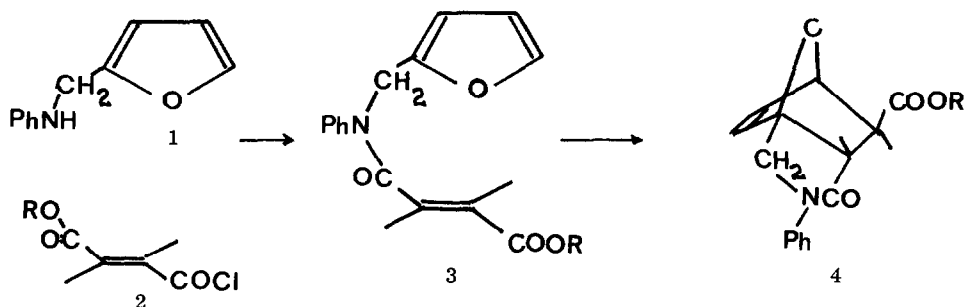
Neil S. Isaacs[†] and Paul Van der Beeke

Department of Chemistry, University of Reading, Reading, RG6 2AD, Berks.

Summary: the intramolecular cyclisation of furans, 3, proceeds with the following activation characteristics: 3(R=Et) has $E_A = 72.5$, $H = 69.9 \text{ kJ mol}^{-1}$, $S^\ddagger = -62 \text{ JK}^{-1} \text{ mol}^{-1}$, $V^\ddagger = -25 \text{ cm}^3 \text{ mol}^{-1}$. The results confirm the existence of a negative volume contribution from the approach of reagents in intermolecular analogues.

Many examples of intramolecular Diels-Alder reactions are now known¹ and are the sources of some unique polycyclic systems. Since high pressures are known to accelerate very markedly intermolecular cycloadditions with volumes of activation and reaction typically lying in the range -30 to $-40 \text{ cm}^3 \text{ mol}^{-1}$ ², it is of interest to know how the intramolecular case compares. The contraction in volume during the activation process is considered to comprise two components: one amounting to some $-10 \text{ cm}^3 \text{ mol}^{-1}$ resulting from the close approach of the reagents and the other due to the formation of two covalent bonds of about $-10 \text{ cm}^3 \text{ mol}^{-1}$ per bond³. It might be surmised that the volume of activation for an intramolecular reaction would lack the first contribution and should therefore be somewhat less negative than for the intermolecular Diels-Alder reaction.

The furan 3, R=H was prepared by a published route⁴. It underwent internal cycloaddition quantitatively and, indeed, rather too readily for some 30-40% of the product 4(R=H) was present in freshly prepared material and the remainder was transformed within a few days even in the solid state. Nonetheless, rates of reaction were obtained and activation parameters calculated (Table). For activation volume measurements, we prepared the corresponding ester, 3, R=Et from 1 and 2 in the presence of triethylamine in ether. This synthesis could be carried out at 0° and within a few minutes. A fresh sample, essentially pure, was prepared for each measurement. The internal cyclisation was followed spectrophotometrically in ethanol at 280nm by the sampling technique previously described⁵.



Rate constants were calculated by a computed least squares fit to an exponential decay curve and are shown in the Table. First-order kinetics were observed to at least 80% reaction.

Table

3, R=Et		3, R=H		3, R=Et	
T/° C	k/10 ² min ⁻¹	T/° C	k/10 ² min ⁻¹	p/bar	k _{rel}
32.6	3.40	41.0	2.37	1	1.00
38.9	5.55	44.0	3.14	370	1.412
47.5	13.3	50.0	5.28	515	1.733
57.5	32.3	55.3	7.96	785	2.46
		57.5	9.60	850	2.51
		60.0	12.12	965	2.61
				1,000	2.93
E [‡] = 72.5		74.2 kJmol ⁻¹		V [‡] = -25 [±] 2 cm ³ mol ⁻¹	
H [‡] = 69.8		71.5 "		V̄ = -23 ± 3 cm ³ mol ⁻¹	
S [‡] = -62		-70 JK ⁻¹ mol ⁻¹			

The volume profile is typical of that for a Diels-Alder reaction with the volume of activation, V^{\ddagger} , very close to the volume of reaction, \bar{V} indicative of a very compact transition state. Of some 50 volumes of activation for Diels-Alder reactions listed in ref. 2, only one is less negative than $-30 \text{ cm}^3 \text{ mol}^{-1}$. This intramolecular analogue, therefore, does proceed with a smaller diminution of volume than its intermolecular counterparts. Nonetheless, the negative value of V^{\ddagger} is a guide that high pressure will be useful in promoting this type of cycloaddition and will be applied on a preparative scale to more reluctant systems than the one examined.

References.

- 1 G. Brieger and J. N. Bennett, Chem. Rev., 1980, **80**, 63.
- 2 T. Asano and W. J. LeNoble, Chem. Rev., 1978, **78**, 207.
- 3 W. J. LeNoble, Prog. Phys. Org. Chem., 1967, **5**, 207.
- 4 D. Bilovic, Croat. Chem. Acta, 1968, **40**, 15.
- 5 N. S. Isaacs, K. Javaid and E. Rannala, J. Chem. Soc., Perkin II, 1973, 709.