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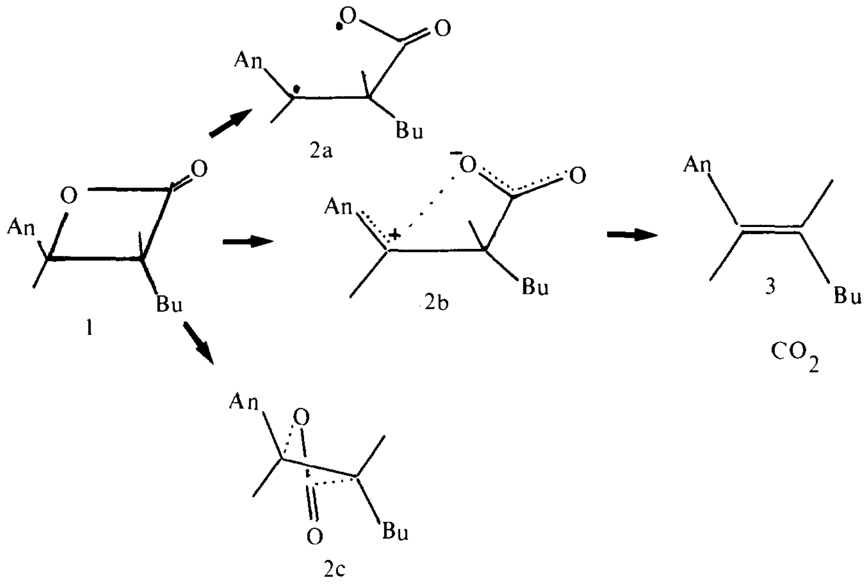
REACTIONS AT HIGH PRESSURE,PART 12;THE VOLUME PROFILE FOR THERMOLYSIS OF A BETA-LACTONE[1].

Neil S.Isaacs
Department of Chemistry,University of Reading,Whiteknights,Reading
and Abdulhameed H.Laila
Department of Chemistry,University of Birzeit,Birzeit,Jordan.

Summary; the volume of activation for thermolysis of the beta-lactone,1, is -28 cm^3mol^{-1} though its volume of reaction is +52. This is consistent with a two step route via a highly dipolar transition state and intermediate 2b.

The thermal decomposition of beta-lactones occurs at moderate temperatures and produces carbon dioxide and an alkene in good yield[2,3]. This procedure has been shown to have synthetic importance since the oxetanone ring can be used as a masked alkene function which will subsequently be decomposed. Moreover, the thermal decomposition is stereospecific, the alkene retaining the same geometry as the parent lactone [4,5]. This is perhaps at first sight surprising since such a result would suggest a concerted process while a concerted (2+2) retro-cycloaddition would require the unfavourable ($_{\pi}2_s+_{\pi}2_a$) geometry (2c) or be symmetry forbidden [6] . On the other hand, evidence has been put forward which suggests the intermediacy of a dipolar intermediate. This is based on the considerable increase in rates of decomposition of oxetanones such as 1 with an increase in solvent polarity. This amounts to a a 438-fold increase on changing the solvent from decalin to formanilide [7]. The mechanism may be formulated as occurring via 2b which loses CO_2 before rotation about the C3-C4 bond can occur, presumably on account of dipolar attractive forces which maintain the configuration. Further support for this pathway may be sought in the volume profile of the reaction. One would predict that the volume of reaction in which two bonds are broken to form neutral products would be similar to that for a retro Diels-Alder reaction, 30-35 $cm^3 mol^{-1}$ while, if the slow step consisted of the breaking of the C4-O bond alone to give a diradical, 2a, the volume change, (i.e. the volume of activation) would be less than half of this quantity. However, heterolytic fission to form 2b would be accompanied by a volume of activation which should be considerably negative due to solvent electrostriction in the vicinity of the charge centres and would be solvent dependent. The volume profile therefore should characterise the reaction pathway.



We prepared 1 according to the procedure of Mulzer [8] as this is one of the most easily decomposed beta-lactams. Its analytical and spectroscopic data were in agreement with the structure,1. Good first-order decomposition rates were obtained at concentrations in the range 10^{-3} to 10^{-4}M,following the progress of the reaction spectrophotometrically at 300 nm and temperatures between 50 and 60. The sole product in quantitative yield was 3. Rates were measured at pressures up to 1 kbar by means of the sampling apparatus previously described[9] and are listed in the Table. .

Table

Rates of Decomposition of 1 as a Function of Pressure

1.solvent;dimethylsulphoxide at 56°;

p/bar;	1	200	300	600	700	900
10^3k_1/min^{-1}	3.20	4.20	4.86	5.80	7.37	8.90

volume of activation $\Delta V^* = -28.5+1$ cm^{3}mol^{-1}

2.solvent;ethanol at 60° ;

p/bar;	1	170	340	700
10^3k_1/min^{-1}	11.0	11.5	13.5	18.8

volume of activation $\Delta V^* = -30 \pm 1$ cm^{3}mol^{-1}

Partial molar volumes of 1 and 3 were determined pyknometrically in DMSO in order to determine the volume of reaction; that for CO_2 was taken as the molar volume.

$\Delta V/cm^3mol^{-1}$	1	185.9
	3	195.8
	CO_2	42

volume of reaction= +52 cm^3mol^{-1}

These results confirm the solvent dependence of the reaction rates and the expected large positive volume of reaction. It is in striking contrast that the volume of activation is both large and negative which can only be explained in terms of a two-step reaction with a dipolar intermediate,2a. The dipolar route,is especially favoured by an oxetanone such as 1 and will not necessarily be the preferred mechanism of thermolysis of all such species.

References

1 Part 11, N.S.Isaacs and H.Abed, J.Chem.Soc.,Perkin II, (1983), in press

2 H.E.Zaugg, Org.Reactions, 6, 305,(1954)

3 Y.Etienne and N.Fischer, 'Heterocyclic Compounds',Vol.XIX, Part 2, A.Weissberger,Ed.Wiley,N,Y,729,(1964).

4 D.S.Noyce and E.H.Banitt, J.Org.Chem.,31,4043,(1966).

5 W.Adam,J.Baeza and J-C.Liu,J.Amer.Chem.Soc.,94,2000,(1972).

6 R.B.Woodward and R.Hoffmann, 'The Conservation of Orbital Symmetry' Verlag Chemie,Weinheim,(1970).

7 J.Mulzer,M.Zippel and G.Bruntrup, Angew.Chemie (Int.Ed.),19, 465, (1980). J.Mulzer,A.Pointer,A.Chucholowski and G.Bruntrup, J.Chem.Soc.(Chem.Comm.),53,(1979).

8 J.Mulzer and M.Zippel, Tetrahedron Letters,751, (1980).

9 N.S.Isaacs,K.Javaid andE.Rannala,J.Chem.Soc.,Perkin II,(1978),

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