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THE KINETICS OF NITROGEN ELIMINATION FROM 4-ALKYLIDENE-$\Delta^{1,2}$-PYRAZOLINES

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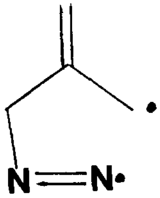

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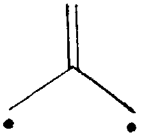

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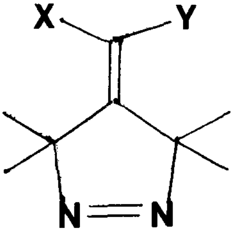

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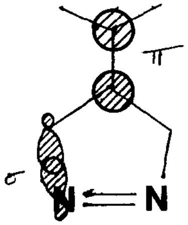

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Recent studies of the pyrolysis of the 4-alkylidene-$\Delta^{1,2}$-pyrazolines[1] suggest that elimination of nitrogen may occur by a stepwise breaking of the carbon-nitrogen bonds, and not, as previously believed,[2] by concerted breaking of both bonds. Whether the first formed intermediate is a diazenyl radical 1 or a TMM 2 it seems reasonable to expect that its formation would be aided by radical stabilising substituents on the double bond. Our studies of the α-methylated systems 3[3] show that this is *not* the case. The kinetics of the reaction in hexadecane were followed by u.v. observation of the N=N n/π^* bond at ca. 325 nm and the results are summarised in the table on the next page. The fairly small spread of reaction rates and lack of any obvious correlation with the substituents' radical stabilising ability could possibly be accomodated by a concerted mechanism but more probably it is stereochemical in origin. In as far as any trends are obvious for the data, the disubstituted systems all eliminate nitrogen slower than the corresponding monosubstituted system and the unsubstituted compound (X=Y=H) is almost fastest of all. The X-Ray crystallographic study reported in the previous paper[4] suggests that, in these α-methylated pyrazolines, the envelope conformation of the 5-membered ring is somewhat flattened so that the π-bond and breaking carbon-nitrogen σ bond(s) are almost orthogonal 4. Furthermore the deuterium scrambling results for the d_6-permethylated system[5] (X=Y=CD_3) suggests that this orthogonal character is largely preserved in the intermediate. Hence, not only is there little initial overlap between the π bond and developing radical centre, but also little likelihood of such overlap developing in the transition state. These results, like those in the accompanying paper, therefore suggest that if these reactions involve initial formation of a TMM intermediate it is of the bis-orthogonal rather than the normally accepted planar or mono-orthogonal type and that if a diazenyl radical is formed that this is also orthogonal in character.

Kinetics of nitrogen elimination

Substituents on **3** X	 Y	k_{rel}(200°)	$\Delta H^{\ddagger}$ (error) kcal mol^{-1}	$\Delta S^{\ddagger}$ (error) cal deg^{-1} mol^{-1}
Me	Me	1.0	44.9 (1.0)	12.6 (0.5)
Cl	Cl	1.9	45.1 (1.1)	14.3 (0.5)
CO_2Et[7]	CO_2Et	6.3	38 (3)	2.0 (0.7)
H	CO_2Et	6.9	41.4 (1.4)	9.0 (0.3)
Ph[7]	Ph	10.5	39.5 (0.8)	5.9 (0.2)
H	Bu^t	15	41.0 (1.2)	9.7 (0.3)
H	Me	16	40.3 (1.5)	8.5 (0.3)
CN	CN	26	39.0 (0.8)	6.7 (0.2)
H[8]	Cl	38	---	---
H	H	61	36.9 (1.0)	4.1 (0.2)
H	Ph	92	38.3 (1.0)	7.6 (0.2)

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R. J. Crawford, H. Tokunaga, L. M. H. C. Schrijver, and J. C. Godard, Canad. J. Chem., 1978, 56, 998.

2 R. J. Crawford, D. M. Cameron and H. Tokunaga, Canad. J. Chem., 1974, 52, 4025.

3 R. J. Bushby and M. D. Pollard, Tet. Let., 1977, 3671.

4 R. J. Bushby, M. D. Pollard, and W. S. McDonald, Tet. Let., accompanying paper.

5 R. J. Bushby and M. D. Pollard, Tet. Let., accompanying paper.

6 The data of P. S. Engel and L. Shen, Canad. J. Chem., 1974, 52, 4040 gives $\Delta H^{\ddagger}$ 38.8 and $\Delta S^{\ddagger}$ 0.5. These authors seem to have studied the reaction over a very narrow temperature range 218-234°. Within this range we have obtained very similar rates and consequently $\Delta G^{\ddagger}$ (38.9 as opposed to 38.5) but over the wider temperature we have employed 170-230 °C, a substantially different value of $\Delta H^{\ddagger}$. As a cross check on our methods we have also studied the decomposition of 7-isopropylidene-2,3-diaza-[2.2.1]bicyclohept-2-ene in acetonitrile and obtained activation parameters essentially the same as those quoted in ref. 1.

7 The u.v. spectrum for this reaction was complicated by product absorptions in the region of interest and the values obtained are thus somewhat less reliable.

8 Vapour phase. S. D. Andrews and A. C. Day, J. Chem. Soc. (B), 1968, 1271.

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