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A CORRELATION OF EASE OF PYROLYTIC *CIS* ELIMINATIONS WITH STRUCTURE[1]

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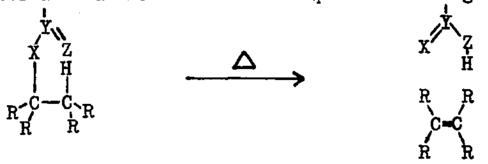
A variety of molecules of type I undergo *cis* eliminations when heated in the vapor or liquid phase. We recently reviewed the mechanistic and synthetic significance of these eliminations,[2] summarizing our views[3,4] that these are highly concerted eliminations with only modest charge separation in the transition state. There are, however, rather large differences in reaction conditions required to bring about the elimination depending upon the atoms X, Y and Z. On the one hand amides (X = NH, Y = C, Z = O) pyrolyze only with the greatest difficulty, requiring temperatures approaching 550°C for even low conversions.[5] Xanthates (X = O, Y = C, Z = S), on the other hand, require temperatures in the



(1)

I

X,Y,Z = C,O,N,S

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[1] This research was supported by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgement is hereby made to the donors of said funds.

[2] C. H. DePuy and R. W. King, *Chem. Rev.* **60**, 431 (1960).

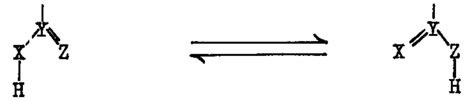
[3] C. H. DePuy, C. A. Bishop and C. N. Goeders, *J. Am. Chem. Soc.* **83**, 2151 (1961).

[4] C. H. DePuy, R. W. King and D. H. Froemsdorf, *Tetrahedron* **7**, 123 (1959).

[5] W. J. Bailey and C. N. Bird, *J. Org. Chem.* **23**, 996 (1958).

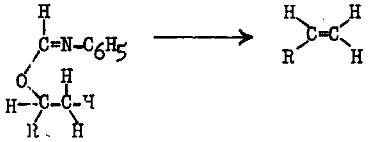
200°C range for elimination.[2,6,7]

Put in the general terms of equation (1), it is seen that a large number of possible combinations may be imagined for this elimination, and it appears worthwhile to put forth a general rule which will allow an estimate to be made of the ease of a given pyrolytic *cis* elimination. *If the equilibrium in equation (2) lies to the right as written, then the pyrolysis represented by equation (1), as written, will proceed readily. If the equilibrium (2) lies to the left, pyrolysis (1) will be difficult.*



(2)

A corollary to this rule is of more use. *If a pyrolysis of the type of equation (1) proceeds only with difficulty, interchange of the atoms X and Y (X ≠ Y) will lead to a system undergoing elimination at much lower temperatures.* The converse also applies. We wish to report a striking example of this corollary. It has already been remarked that amides require very high temperatures for pyrolytic elimination. Interchange of the nitrogen and oxygen gives rise to imino ethers. *These compounds undergo pyrolytic cis eliminations at 350-400°C,*[7] two hundred degrees lower



(3)

than amides. An even more instructive example is found in enol ethers ($X = O$, $Y = C$, $Z = CH_2$) which undergo pyrolytic eliminations more readily than esters.[3] Interchange of X and Y gives ketones, which do not

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[6] H. R. Nace, *Organic Reactions*, A. C. Cope, Ed., J. Wiley and Sons, Inc., New York, Vol. 12, p. 57.

[7] K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.* *77*, 2207 (1955) noted the thermal lability of the 2-butyliminoether.

eliminate. In this system the acetate might serve as a standard, since X = Y. Then the enol ether pyrolysis goes more easily than the acetate pyrolysis because there is additional energy to be gained in the conversion represented by (2).[6] The rule also explains why xanthates are more reactive than thiolcarbonates in these eliminations.[8]

In the cases studied so far, the rule may be applied to the pyrolytic elimination of oxides (equation 4). A pyrolytic elimination as in equation (4) will proceed readily in those cases (amine oxide,[9] sulfoxide[10])

(4)

(5)

in which the equilibrium (5) lies to the right, and will be difficult (phosphine oxide[11]) when the equilibrium (5) lies to the left.

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[8] E. Salomara, Ann. Acad. Sci. Fennicae, Ser. II 94, 1 (1959).

[9] A. C. Cope in Organic Reactions, J. Wiley and Sons, Inc., New York, Vol. II, p. 317

[10] C. A. Kingsbury and D. J. Cram, J. Am. Chem. Soc. 82, 1810 (1960).

[11] W. J. Bailey and W. M. Muir, Abstracts of Paper, 140th Meeting American Chemical Society, Chicago, Illinois, 1961, p. 36Q.