On Anchimerically Assisted Homolysis *via* Sulphide Functions

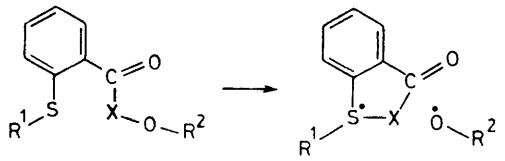
By ALEXANDER J. LAWSON

(*Institut für Organische Chemie der Universität Mainz, Johann-Joachim-Becher-Weg* 18, *D*-6500 *Mainz, Federal Republic of Germany*)

Summary In contrast to O–O fission, anchimeric assistance from sulphide functions in the rate of unimolecular fission of the N–O bond is only marked for heterolysis reactions; analogous homolyses are very much less accelerated, although bridged radical intermediates are involved.

THE thermolysis of *ortho*-substituted peresters[1] such as (**1a**, **b**) to yield the corresponding radical-pairs[2] (**2**) has long been regarded as an outstanding example of anchimerically accelerated homolysis, despite possible alternative explanations[3] for the 10^4—10^6-fold rate increase compared to model compounds, such as the corresponding *para*-isomers or unsubstituted perbenzoates.

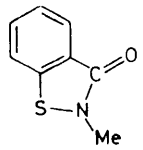
The present report describes the thermolysis of the analogues (**1c**, **d**), where the N–O bond undergoes homolysis[4] and the nature of the products clearly indicates a bridged intermediate free radical, but where the anchimeric effect produces no acceleration (a slight deceleration was observed), and where the effect of increasing solvent polarity is very small or even negative (*cf.* Ref. 1). Thus the thermolysis of (**1d**) in CCl_4 at 78 °C yields (**3**) (55%)[5] along



(1) (2)

	a	**b**	**c**	**d**
R^1	Ph	Me	Me	Bu^t
X	O	O	NMe	NMe
R^2	Bu^t	Bu^t	C(:S)NMe$_2$	C(:S)NMe$_2$

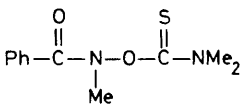
with products directly stemming from the t-butyl radical (t-butyl chloride, 20%),[6] and from radical addition of the solvent to isobutene [(**4**), 28%],[7] at a rate which is *ca.* 4 times slower than the rate of homolysis[4] of (**5**) to the isomer (**6**) and the amide (**7**). Polar solvents slow the rate of homolysis of (**1d**) still further; similar rates were found for compound (**1c**).



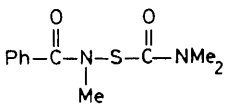
(3)

$Me_2C(Cl)-CH_2-CCl_3$

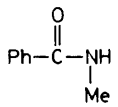
(4)



(5)



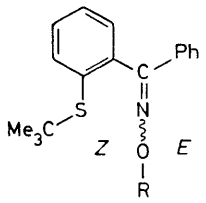
(6)



(7)

A dramatic acceleration (*ca.* 10^4) of the rate of N–O fission is only observed when the process is heterolytic, leading to an ion-pair. Thus the thermolysis of (**8a**) (*E*-isomer) in methanol ($t_{1/2}$ 1 h at 65 °C) proceeds several hundred times faster than in hexane, and yields the benzisothiazole (**9**) (82%) accompanied by the t-butyl cation, which is trapped by the solvent to give Bu^{t}OMe (75%). Control experiments showed that the ether did not arise from isobutene. The *Z*-isomer (**8b**) reacts *ca.* 10^4 times slower.

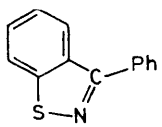
In contrast, the homolytic[8] decompositions of (**8c**) and (**8d**) are only slightly accelerated compared to the corresponding unsubstituted benzophenone oxime *O*-thiocarbamate,[9] factors of 30—60 and 1—3 being observed respectively, and no great effect of solvent polarity on the rate was observed. The benzisothiazole (**9**) forms a significant product for both (**8c**) and (**8d**). ^{13}C-C.I.D.N.P. effects were observed in the product (**9**) [from (**8d**)], even in the polar solvent [$^2H_6$]dimethyl sulphoxide.



(8)

	a	**b**	**c**	**d**
Configuration	*E*	*Z*	*E*	*Z*
R	C(:O)Ph	C(:O)Ph	C(:S)NMe$_2$	C(:S)NMe$_2$

These results may be summarised as follows. (a) The reaction of (**8a**) to yield an ion-pair shows kinetic behaviour strongly similar to that observed[1] for (**1a**, **b**), *i.e.* a large anchimeric effect and an acceleration in polar solvents. The stereochemical requirements are as expected for a nucleophilic substitution, *i.e.* backside attack. (b) The homolyses of (**1c**, **d**) and (**8c**, **d**) result in a very marked reduction of both the rate acceleration and the effect of solvent polarity; furthermore the requirement for backside attack is relaxed.



(9)

While the degree of reaction endothermicity probably plays a role in determining the extent of bond-formation in the transition state, these results nevertheless clearly

show that anchimeric assistance in this series of hydroxylamine derivatives cannot be associated with the homolysis reaction to any very marked extent, the effects being noteworthy only when an ion-pair intermediate results.

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