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STEREOCHEMISTRY AND KINETICS OF IMIDATE PYROLYSIS

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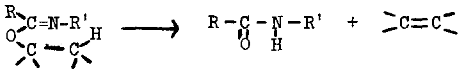
The thermal rearrangement of O-aryl and O-allyl imidates to disubstituted amides (Chapman rearrangement) is a well known reaction (1). However, the pyrolysis of O-alkyl imidates to a monosubstituted amide and olefin has only recently been systematically investigated (2). These previous results have demonstrated the generality and synthetic usefulness of the reaction as well as the lower temperature necessary for olefin formation relative to acetate pyrolysis.



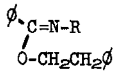
We now report our initial stereochemical and kinetic results which establish that imidates undergo elimination by a unimolecular cis process. The stereochemical data on the vapor phase pyrolysis of the N-phenylbenzimidates of cis and trans 2-phenylcyclohexanol (3) are listed below.

TABLE I

	T°C	%1-olefin	%3-olefin
trans	375	84.8	15.2
trans	500	80.5	19.5
cis	535-560	15.4	84.6
cis	465	14.9	85.1

The predominant formation of 3-phenylcyclohexene from pyrolysis of the imidate of the cis alcohol demonstrates that the reaction proceeds by a preferential cis elimination. In addition, the olefin distributions obtained are very similar to those reported from the corresponding xanthates or acetates (4).

The kinetics of the decomposition of Ia and Ib in diphenylether were

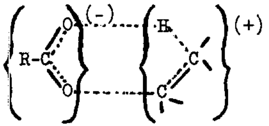


$\phi\text{-C(=N-R)-O-CH}_2\text{CH}_2\phi$

Ia, $R{=}CH_3$
Ib, $R{=}C_6H_5$

examined and a first order rate law was obeyed by each for greater than 90% of reaction.

It is generally agreed that the major factor influencing the rate of ester pyrolysis is the lability of the alkyl carbon-oxygen bond rather than the nucleophilicity of the carbonyl oxygen (5). Indeed the transition state to best accommodate the experimental facts has been represented as



This explains for example the larger pyrolysis rate of haloacetate relative to unsubstituted acetates even though the nucleophilicity of the carbonyl oxygen is diminished.

A similar representation for imidate pyrolysis would predict that Ib undergo elimination at a faster rate than Ia since substitution of phenyl for methyl should increase the lability of the O-C bond (although decrease the nucleophilicity of the imino nitrogen). This, however, was found not to be the case. At 245° Ia undergoes elimination 2.8 times faster than Ib. This reversal cannot be attributed to Ib having a more negative $\Delta S^{\ddagger}$ than Ia as is seen in the following table. Furthermore, if the activation entropy or log A were the same for Ia and Ib, then the 6 Kcal difference in experimental activation energy would result in Ia reaction about 150 times faster at 245° than Ib.

TABLE II

	Ea	Log A	$\Delta S^{\ddagger}$
Ia	34.6	12.6	-12.1
Ib	40.6	14.7	- 2.6

This result demonstrates than in the case of imidates, the nucleophilicity of the attacking atom plays an important and perhaps dominant role. In terms of the transition state, the results reported suggest that there is a greater degree of bonding between the attacking atom and the β hydrogen in imidates than in acetates.

It should be noted that application of the general rule proposed by DePuy (6) to estimate the ease of pyrolytic cis elimination correctly predicts the greater reactivity of Ia relative to Ib. It is reasonable that of the two equilibria,

(1)

(2)

eq.(2) would lie further to the right. Translating these thermodynamic guidelines into kinetic considerations require that the transition state be far along the reaction coordinate. This is consistent with the proposed important involvement of the attacking atom in the transition state for imidate pyrolysis.

It might be argued that the observed kinetics are those of a rate determining syn-anti imidate isomerization which preceeds the elimination step. Although the stereochemistry of imidates has not been studied, the interconversion of such geometric isomers is probably very rapid, with an expected activation energy of less than 20 Kcal/M. The basis for this is that compounds of the type $Ar_1\ Ar_2C{=}N{-}Ar$ have isomerization Ea values of *ca*. 20 Kcal/M (7) while those of iminocarbonates, $(CH_3O)_2C{=}N{-}Ar$, are 13-16 Kcal/M. (8) In addition, we find the specific rate constant for the isomerization of the iminocarbonates at 60° is 10^7 times larger than that for decomposition of Ib at 245°. Therefore, it is safe to assume that the rate determining step for imidate pyrolysis is the one which results in olefin formation.

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