The Thermal Decomposition of Amine Imides

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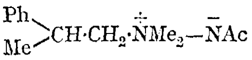
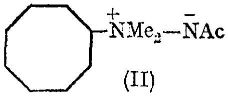
IT has been shown that amine oxide pyrolyses proceed almost exclusively *via* a *cis*-elimination,[1] and that Hofmann eliminations of quaternary ammonium compounds can, in certain cases, proceed, at least in part, through a *cis*-elimination.[2] Both reactions are considered to occur *via* five-membered cyclic transition states.

In the present work thermal decompositions have been carried out on *NN*-dimethyl-2-phenylpropylamine acetimide (I) and *NN*-dimethylcyclo-octylamine acetimide (II). When (I) (with a trace of hydroquinone) and (II) were heated at 125° *in vacuo* the respective olefins, 2-phenylpropene (79%) and cyclo-octene (82%) were isolated. The cyclo-octene was found to consist of 96·5% *cis*- and 3·5% *trans*-cyclo-octene by gas chromatographic

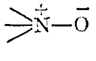


$Ph(Me)CH{\cdot}CH_2{\cdot}\overset{+}{N}Me_2-\overset{-}{N}Ac$

(I)

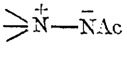


(II)



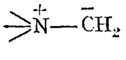
$\geqslant\overset{+}{N}-\overset{-}{O}$

(III)



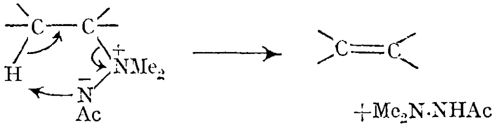
$\geqslant\overset{+}{N}-\overset{-}{N}Ac$

(IV)



$\geqslant\overset{+}{N}-\overset{-}{C}H_2$

(V)



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analysis on di-isodecyl phthalate under conditions where no isomerisation occurs.† This compares with pure *cis*-cyclo-octene from amine oxide pyrolysis[3] and *ca.* 85 : 15 *cis*- : *trans*-cyclo-octene from Hofmann elimination with phenyl-lithium.[4] The only other isolable product was 2-acetyl-1,1-dimethylhydrazine which was characterised by comparison with an authentic sample.[5]

The olefins can most reasonably be considered to arise from a concerted *cis*-elimination involving a five-membered transition state (Scheme). Such a mechanism fills an isoelectronic gap in a series of dipolar part structures (III) → (V) capable of effecting a pyrolytic *cis*-elimination. It is not possible at present to rule out a *cis*-elimination involving the oxygen end of the ambident anion. However such a process involving a seven-membered transition state is considered less likely. Two other types of pyrolytic decomposition of amine-imides are possible, *viz.* a Stevens rearrangement,[6] and initial isocyanate formation.[7] These processes have only been observed in structures with alkyl residues not containing β hydrogens and at higher temperatures.

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