Pyrolysis of 3,5-Diphenyl-1,2,4-oxadiazole and 2,5-Diphenyl-1,3,4-oxadiazole

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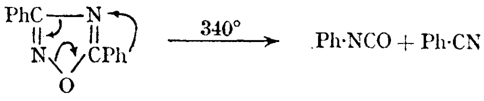
STRONG similarities often exist between the thermal decomposition reactions of molecules and those brought about by electron impact in the mass spectrometer.[1-3] We have examined the decomposition reactions of 3,5-diphenyl-1,2,4-oxadiazole (I) and 2,5-diphenyl-1,3,4-oxadiazole (II) induced thermally, and have compared them with those brought about by electron impact.[4] Although some striking similarities are apparent between these processes in the case of (I), those for (II) do not correlate well.

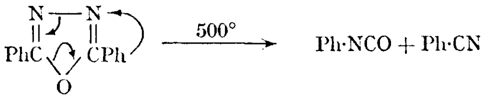
Compounds (I) and (II) in 5—20 mg. quantities were pyrolysed for two hours at 340° and 500° respectively in sealed glass ampoules evacuated to a residual pressure of 10^{-4} torr. The only products detected by gas–liquid chromatography using a flame-ionization detector, were phenyl isocyanate and benzonitrile which were quantitatively determined by this method. Undecomposed (I) and (II) were not eluted from the column (silicone oil impregnated on Chromosorb P) at the temperature of these experiments, and were only slowly removed at 250°.

Mass-spectrometric (MS2-H) examination of the reaction mixtures identified the principal components as phenyl isocyanate, benzonitrile, and undecomposed (I) or (II); carbon dioxide was also detected and at least one compound responsible for a low-intensity mass-spectral peak at m/e 194.

The most likely thermal breakdown schemes appear to be:



(I) Scheme 1



(II) Scheme 2

However, the molar product ratios (mean of four pyrolysis experiments in each case) of benzonitrile to phenyl isocyanate were 1·4 ± 0·2 for (I) and 1·2 ± 0·1 for (II). These deviations from the 1 : 1

molar product ratios expected from Schemes 1 and 2 can be rationalized on the basis of a concomitant reaction of phenyl isocyanate to give diphenylcarbodi-imide and carbon dioxide,

$$2\text{Ph·NCO} \rightarrow \text{PhN:C:NPh} + \text{CO}_2$$

which is known[5] to take place in sealed tubes at 280° and which has been shown to be an equilibrium process lying far on the side of unchanged phenyl isocyanate.[6] This reaction of phenyl isocyanate also accounts for the carbon dioxide found in the pyrolysis products, and the peaks at m/e 194 in the mass spectra of the pyrolysis products of (I) and (II) might correspond to the diphenylcarbodi-imide molecular ion.

On the basis of a 1 : 1 stoicheiometry between starting material and benzonitrile (Schemes 1 and 2) it was estimated that about 40% of (I) and 80% of (II) had decomposed in these experiments.

Phenyl isocyanate and benzonitrile produced by pyrolysis of (I) correlate with the strong fragment-ion peaks at m/e 119 (PhNCO^+) and 103 (PhCN^+) in the mass spectrum[4] of this compound. However, in the case of (II) the principal mass-spectral fragment-ion peaks are at m/e 165, 105, and 77, while the peaks at m/e 119 and 103 are only of low intensity. The high-intensity fragment ions probably arise by the expulsion of molecular nitrogen from the molecular ion of (II),[4] but no evidence was found for the occurrence of a comparable process in the thermal breakdown of this molecule.

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[1] F. W. McLafferty, "Mass Spectrometry of Organic Ions", Academic Press, London, 1963, p. 311.

[2] H. M. Grubb and S. Meyerson, Reference 1, p. 522.

[3] E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.

[4] J. L. Cotter, *J. Chem. Soc.*, 1964, 5491.

[5] R. Stolle, *Ber.*, 1908, **41**, 1125.

[6] T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Amer. Chem. Soc.*, 1962, **84**, 3673.