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AN INTERESTING FRAGMENTATION DURING THE THERMOLYSIS OF AZIDO ISOXAZOLES

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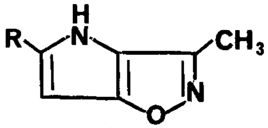
Summary: Thermolysis of azido isoxazoles has been found to give cinnamoyl cyanides formed by facile fragmentation of the isoxazole ring.

The deoxygenative cyclisation of suitably substituted nitro aromatics with tervalent phosphorous compounds and thermal decomposition of aryl vinyl azides have been exploited in recent years for constructing nitrogen heterocycles[1,2].

In our efforts to synthesise the hitherto unreported pyrroloisoxazole ring system 1 from the azido isoxazole 3 we have encountered an interesting fragmentation reaction.



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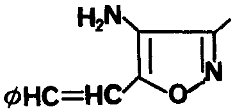

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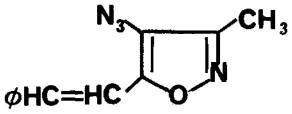

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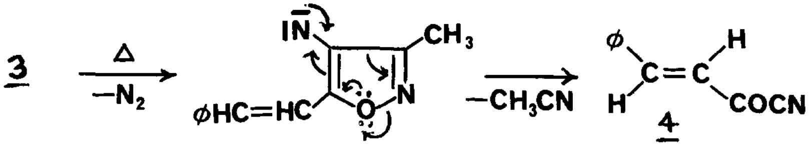
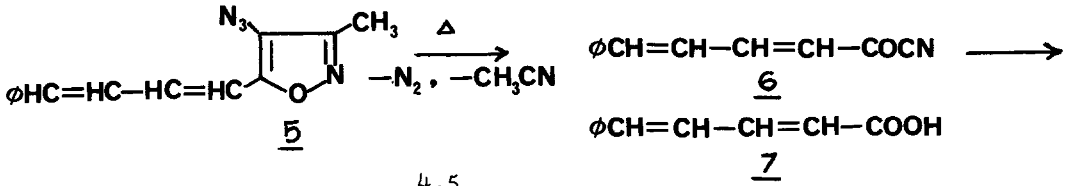
The azido isoxazole 3 (m.p. 88-89°C) was prepared by standard procedure from the reported[3] amino isoxazole 2; its thermolysis in refluxing decalin for one hour followed by work up furnished cinnamoyl cyanide 4 in 90% yield and none of the expected product 1 (R=Ph). The formation of the cinnamoyl cyanide 4 can be rationalized as follows:



The thermolysis of the azido isoxazole 5 (m.p. 124-125°C) was studied with a view to find out whether the presence of an extra double bond might favour the formation of a nitrene insertion product. In this case also the nitrile 6 (confirmed by hydrolysis to 5-phenyl-2,4-penta dienoic acid) was obtained as the sole product.



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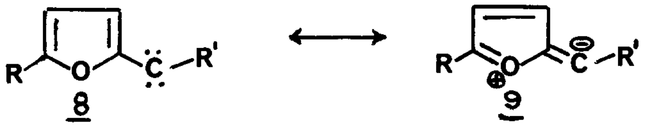
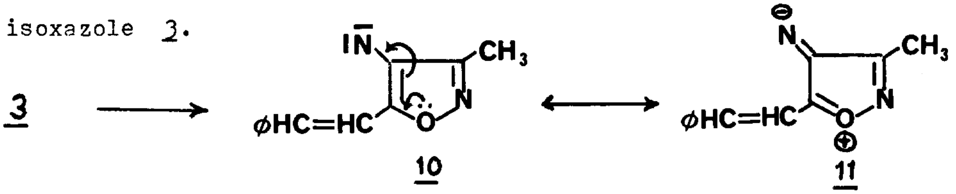
Recently, Schechter et al[4,5] have studied the vacuum pyrolysis of diazo(2-furyl) methanes and diazo(5-isoxazolyl) methanes. Contribution of delocalization as in 8 and 9 has been invoked in the case of furan to rationalize the products formed.



8 9

In the present instance also, contributions by structures 10 and 11 similar to the one depicted may be invoked to explain the fragmentation of the isoxazole 3.



10 11

A number of other azido isoxazoles bearing different substituents in the aromatic nucleus were found to behave similarly on thermolysis yielding the corresponding cinnamoyl cyanides. We are currently investigating the photochemistry of these azides.

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References:

* To whom all correspondence should be addressed.

All the new compounds reported in this paper gave satisfactory spectral (NMR and IR) data and elemental analysis.

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