The 1,4-Hydrogen Shift in Nitrile Ylides

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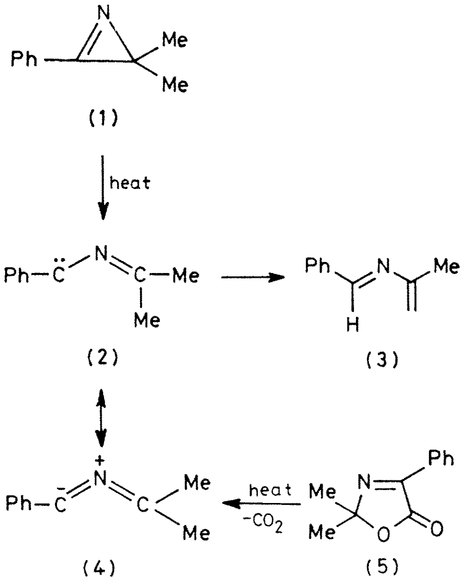
Summary 2-Azabutadienes are formed in quantitative yield by flash vacuum pyrolysis of oxazol-5(2*H*)-ones, but partially decompose owing to chemical activation when generated from 2*H*-azirines.

THE thermolysis of 2,2-dimethyl-3-phenyl-2*H*-azirine (**1**) in the gas phase at atmospheric pressure has been reported to give the azabutadiene (**3**) in 24% yield.[1] This, together with other, similar reactions[1-3] is evidence for C–C bond cleavage leading to the iminocarbene (**2**). Since theoretical calculations[4] indicate that iminocarbenes are only one of the canonical forms of the ground state of nitrile ylides (**4**), it would be expected that the generation of (**4**) in the gas phase would also lead to (**3**).



It is known that solution thermolysis of 2,2,4-trisubstituted oxazol-5(2*H*)-ones affords nitrile ylides which can be trapped inter- or intra-molecularly.[3] We have now examined the flash vacuum pyrolysis of (**5**) and found that CO_2 is extruded in the temperature range 400—600 °C (10^{-4} Torr). The only other product was the azabutadiene (**3**), formed in 50% yield together with 50% of (**5**) at 400 °C, and in virtually quantitative yield at 600 °C (90% isolated yield; only traces of impurities detectable by t.l.c.).

Since Wendling and Bergman obtained large amounts of the decomposition products of (**3**) (acetonitrile, styrene, and polymer) in the pyrolyses of (**1**) above 472 °C, we reinvestigated the pyrolysis of (**1**) in our system. At 500 °C ($<10^{-3}$ Torr) only (**1**) was recovered. At 600 °C, a mixture of (**1**), styrene, and acetonitrile (33·5:38·5:28) together with traces of (**3**) was obtained. At 700 °C, the starting material (**1**) had almost completely disappeared, (**3**) was no longer detectable, and styrene and acetonitrile were formed in a stoicheiometric ratio (51·2:48·8).

From these results, the following conclusions can be drawn: (i) the activation energy for ring opening of (**1**) is higher than that for fragmentation of (**5**); (ii) (**3**) is stable when formed from (**5**) at 600 °C, but largely decomposes when formed from (**1**) at the same temperature and pressure. The most reasonable explanation of this behaviour is that the azabutadiene (**3**) is chemically activated[5] when formed from (**1**), but relatively 'cold' when formed from (**5**). This is due to the higher heat of formation of (**1**), together with the higher energy of activation for its reaction. This hypothesis was confirmed by performing the pyrolysis of (**1**) at 600 °C in the presence of 1 Torr of N_2 as carrier gas, serving to deactivate the 'hot' (**3**). The yield of (**3**) rose to 10% under these conditions.

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