Evidence for a 1,3-Sigmatropic Rearrangement of a Nitrile *N*-Benzylimide to a *C*-Benzyl-substituted Diazoalkane

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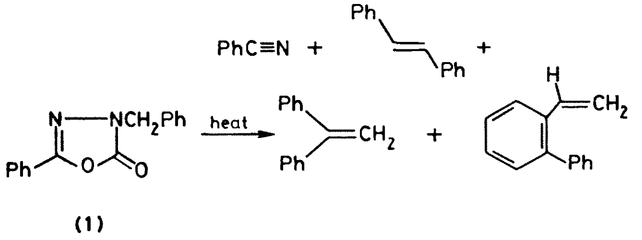
Summary The flash vacuum pyrolysis of *N*-benzyl-2-phenyl-1,3,4-oxadiazolin-5-one generates a nitrile *N*-imide which rearranges to a diazoalkane *via* a 1,3-sigmatropic benzyl shift.

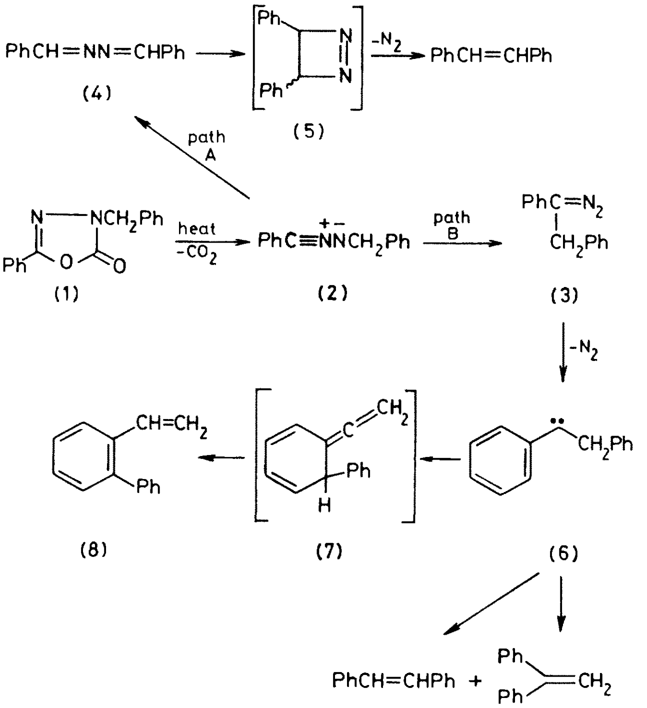
The synthetic usefulness of the 1,3-dipolar cycloaddition reactions of nitrile *N*-imides has been described in numerous papers.[1] These reactive 1,3-dipoles have been generated by the thermal decomposition of 2,5-disubstituted tetrazoles,[2] by the photolysis of sydnones,[3] and by the base-induced elimination of hydrogen halide from hydrazonoyl halides.[4] The thermolysis of 1,3,4-oxadiazolin-5-ones in the gas phase or in inert solvents also gives nitrile *N*-imides which, in the absence of trapping agents, undergo intramolecular reorganization.[5,6] We now report that the nitrile *N*-benzylimide (**2**), derived from the pyrolysis of (**1**), undergoes a previously undetected rearrangement *via* a novel 1,3-sigmatropic shift to produce the *C*-benzyl-substituted diazoalkane (**3**).

Flash vacuum pyrolysis (f.v.p.) of 3-benzyl-5-phenyl-1,3,4-oxadiazolin-2-one (**1**) at 700 °C (10^{-2} Torr) gave benzonitrile (15%), *cis*- and *trans*-stilbene (5 and 42%, respectively), 1,1-diphenylethylene (12%), and *o*-phenylstyrene (18%) as the major products (Scheme 1). The structures of the thermal products were assigned unambiguously by comparison with independently synthesized samples.



Scheme 1.

Formation of these products requires bonding, at some point in the reaction, between the C-5 of the oxadiazolin-2-one ring and the benzylic carbon atom. A number of reaction sequences can explain these observations. One reasonable rationalization of the formation of *cis*- and *trans*-stilbene (path A) involves the diazetine intermediate (**5**) formed from benzaldehyde azine (**4**). This path is akin to the 1-phenylazabutadiene–azetine-styrene thermal conversion reported by Wendling and Bergman.[7] Since Wentrup and Fischer have isolated an azine from the pyrolysis of 3-methyl-5-phenyloxadiazolin-2-one,[8] we decided to investigate the pyrolysis of benzaldehyde azine (**4**) in our system. At 700 °C (10^{-2} Torr), a mixture of benzonitrile (90%) and *trans*-stilbene (10%) was obtained. It should be noted that *trans*-stilbene is formed in much greater quantities than benzonitrile in the f.v.p. of the oxadiazolinone (**1**). Although we cannot rule out path A, the large amount of benzonitrile formed in the thermolysis of (**4**) suggests that this route represents a minor process for the formation of the stilbenes.



Scheme 2.

The pyrolysis results described above are best interpreted according to Scheme 2. The first step involves the loss of carbon dioxide to generate the nitrile *N*-imide (**2**). This species undergoes a subsequent 1,3-sigmatropic benzyl shift to give the diazoalkane (**3**) (path B). The products obtained are most simply explained by invoking the loss of nitrogen to generate a carbene intermediate (**6**) followed by either hydrogen or phenyl migration. At the high temperatures employed, the carbene (**6**) also undergoes a novel 1,4-phenyl shift to give the intermediate (**7**) which readily tautomerizes to the observed styrene derivative. Independent work by Wentrup and Fischer[8] suggests that the activation energy associated with the 1,3-sigmatropic benzyl shift is lower than that for a 1,4-hydrogen shift. This would account for the variation of products obtained from the thermolysis of *N*-substituted oxadiazolin-2-ones.

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