

The Thermal Decomposition of 1-Methyl-1,2,3-benzotriazin-4(1*H*)-one: Matrix Isolation of the Reactive Intermediates

Ian R. Dunkin,^{*a} Michael A. Lynch,^a Robert Withnall,^a A. J. Boulton,^{*b} and Neil Henderson^b

^a Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, U.K.

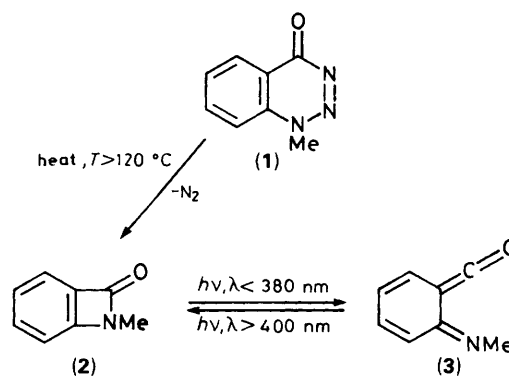
^b School of Chemical Sciences, University of East Anglia, University Plain, Norwich NR4 7TJ, U.K.

Thermal decomposition of 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (**1**) above 120 °C gave rise to 1-methylbenzazetinone (**2**), which was trapped in solid argon at 15 K; near-UV irradiation of (**2**) converted it partially into its iminoketene isomer (**3**), and the reverse conversion of (**3**) into (**2**) was effected with longer wavelength irradiation.

A recent paper from one of our laboratories described the synthesis of 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (**1**).¹ This compound might be expected to decompose readily by loss of dinitrogen, yielding either the iminoketene (**3**) or its valence tautomer, the benzazetinone (**2**). It was actually found to be surprisingly stable. Thus, although (**1**) was found to be somewhat photosensitive, it did not melt or undergo obvious decomposition below 320 °C. In order to investigate further the chemistry of (**1**), and in the hope of observing one or both of the reactive species (**2**) and (**3**), we have carried out a study of the decomposition of (**1**) using low-temperature matrix-isolation as a means of trapping the products.

We now report that when thermolysis of the solid benzotriazinone (**1**) above 120 °C was carried out under a stream of argon, a product (**2**) was formed, which could be trapped in a matrix by condensation of the resulting gas mixture on a CsI or CaF₂ window at 15 K.² The initial product (**2**) was characterized by a strong carbonyl absorption at 1843 cm⁻¹ (Figure

1a) and near-UV absorptions in the region $\lambda < 380$ nm (Figure 2a). It was identified as 1-methylbenzazetinone by comparison of its absorptions with the reported carbonyl stretching



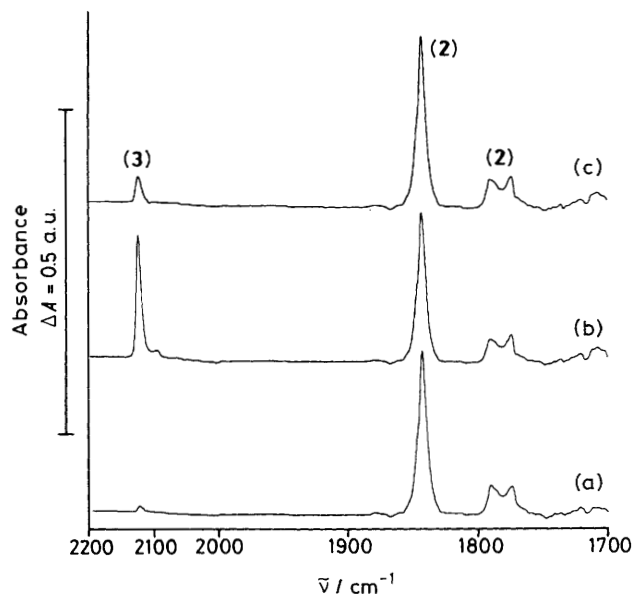


Figure 1. IR spectra in the 1700–2200 cm^{-1} region of reactive thermal decomposition products of 1-methyl-1,2,3-benzotriazin-4(1H)-one (**1**) in solid argon at 15 K: (a) immediately after deposition, (b) after 2.5 h irradiation of the sample at 280 ± 5 nm, and (c) after a further 0.5 h irradiation of the sample at 500 ± 5 nm. [The bands of (**2**) at 1775 and 1790 cm^{-1} are probably due to overtones or aggregates of (**2**).]

absorptions of 1-ethyl- and 1-t-butyl-benzazetinones at 1805 and 1799 cm^{-1} ,^{3†} respectively, and the near-UV absorptions of the 1-t-butyl compound at 222, 273, and 370 nm.³

A very weak band at 2125 cm^{-1} was present on deposition and grew markedly upon near-UV irradiation ($\lambda < 380$ nm) of the matrix, with concomitant decrease in the 1843 cm^{-1} band (Figure 1b). We attribute the 2125 cm^{-1} band to $\nu(\text{C}=\text{C}=\text{O})$ of the iminoketene (**3**), which, so far as we know, has not previously been observed spectroscopically. An analogous

† The 1843 cm^{-1} band for the 1-methyl compound in solid argon is $\sim 40 \text{ cm}^{-1}$ higher than the $\text{C}=\text{O}$ stretching bands for the 1-ethyl and 1-t-butyl compounds in CH_2Cl_2 solutions. This is expected, as stretching frequencies are commonly higher in argon than in CCl_4 , CH_2Cl_2 , and CHCl_3 , owing to solvent shifts. For a general discussion of this effect, see A. J. Barnes, in 'Vibrational Spectroscopy of Trapped Species,' ed. H. E. Hallam, Wiley, London, 1973, ch. 4.

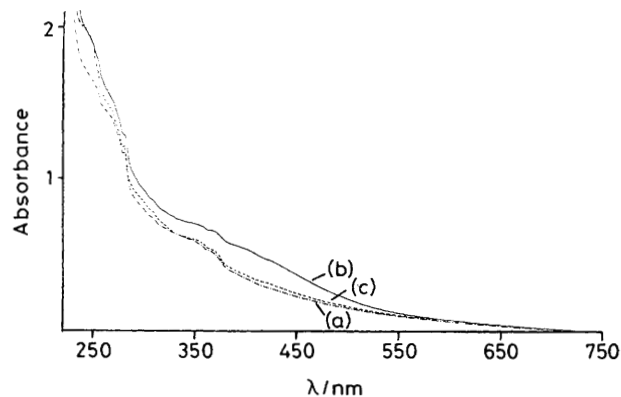


Figure 2. Optical absorption spectra in the 250–750 nm region of the same sample as in Figure 1: (a) immediately after deposition, (b) after 2.5 h irradiation at 280 ± 5 nm, and (c) after a further 0.5 h irradiation at 500 ± 5 nm.

ketoketene absorption at 2139 cm^{-1} has been observed during a matrix isolation study of benzoxet-2-one.⁴ In addition to the 2125 cm^{-1} band, a very broad UV absorption centred at about 420 nm was observed to grow at about the same relative rate, and this is also attributed to (**3**) (Figure 2b). Irradiation into this absorption with light of $\lambda > 400$ nm reconverted the iminoketene (**3**) into its benzazetinone isomer (**2**) (Figures 1c and 2c).

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References

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- 2 The matrix isolation equipment has been described fully by I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2079. Research grade argon of better than 99.9997% purity was obtained from BOC Ltd. IR spectra were recorded on JASCO model IRA-2 and Perkin Elmer model 684 spectrometers, the latter interfaced with a Perkin Elmer model 3600 data station; UV-visible spectra were recorded on a Shimadzu model UV250 instrument.
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