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

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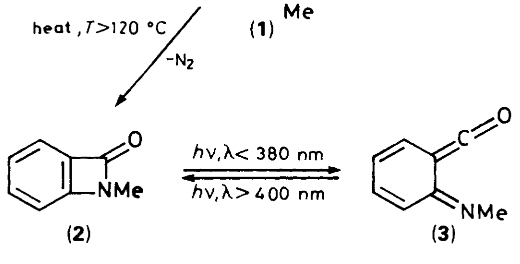
Thermal decomposition of 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (**1**) above 120 °C gave rise to 1-methylbenzazetinone (**2**), which was trapped in solid argon at 15 K; near-UV irradiation of (**2**) converted it partially into its iminoketene isomer (**3**), and the reverse conversion of (**3**) 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 CaF_2 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 λ <380 nm (Figure 2a). It was identified as 1-methylbenzazetinone by comparison of its absorptions with the reported carbonyl stretching



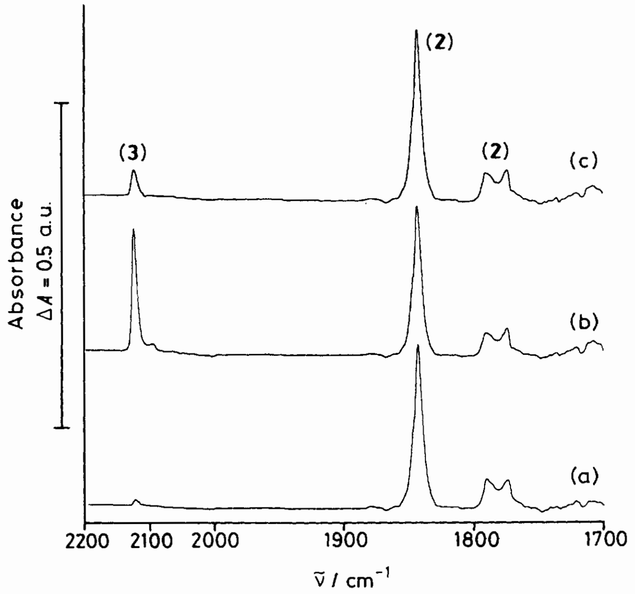


Figure 1. IR spectra in the 1700—2200 cm^{-1} region of reactive thermal decomposition products of 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (**1**) in solid argon at 15 K: (a) immediately after deposition, (b) after 2.5 h irradiation of the sample at 280 ± 5 nm, and (c) after a further 0.5 h irradiation 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 (λ <380 nm) of the matrix, with concomitant decrease in the 1843 cm^{-1} band (Figure 1b). We attribute the 2125 cm^{-1} band to ν(C=C=O) of the iminoketene (**3**), which, so far as we know, has not previously been observed spectroscopically. An analogous 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 λ > 400 nm reconverted the iminoketene (**3**) into its benzazetinone isomer (**2**) (Figures 1c and 2c).

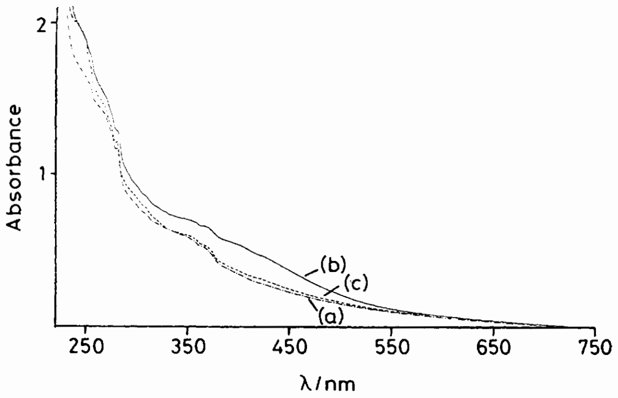


Figure 2. Optical absorption spectra in the 250—750 nm region of the same sample as in Figure 1: (a) immediately after deposition, (b) after 2.5 h irradiation at 280 ± 5 nm, and (c) after a further 0.5 h irradiation at 500 ± 5 nm.

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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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† The 1843 cm^{-1} band for the 1-methyl compound in solid argon is ~40 cm^{-1} higher than the C=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.