Tetrahedron Vol. 45, No. 1, pp. 259 to 268, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

THE PHOTOCHEMISTRY OF 1,4-DIHYDRO-5H-TETRAZOLE DERIVATIVES ISOLATED IN LOW-TEMPERATURE MATRICES

Ian R. Dunkin,* and Charles J. Shields
Department of Pure and Applied Chemistry, University of Strathclyde,
295 Cathedral Street, Glasgow G1 1XL, U.K.

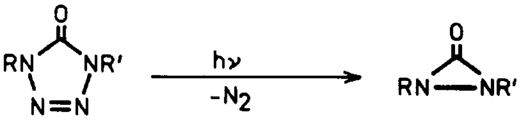
and Helmut Quast
Institut für Organische Chemie, Universität Würzburg, Am Hubland,
D-8700 Würzburg, W. Germany

(*Received in UK* 21 *September* 1988)

Abstract: Six 1,4-dihydro-5H-tetrazole (tetrazoline) derivatives have been photolysed in Ar and N_2 matrices at 12 K. The dimethyltetrazolinone (1a) gave as the major product the same diaziridinone obtained previously from solution photolysis, but it also underwent a novel cleavage to MeNCO and, presumably, methyl azide. Iminotetrazolines (3a) and (3b) gave the corresponding carbodiimides (5a) and (5b), and iminodiaziridines (4a) and (4b); while the tetrazolinethiones (7a) and (7b) gave carbodiimides (8a) and (8b), respectively. Photolysis of the vinyl substituted tetrazolinone (9) proceeded differently in inert ambient-temperature solutions and low-temperature matrices. In the former an imidazolone (10) was the sole isolable product, while in the latter formation of diaziridinone (15) competed with an alternative cleavage giving t-butyl isocyanate and vinyl azide. These results are best interpreted on the basis of an intermediate biradical, which, however, could not be detected directly by matrix ir. spectroscopy.

Photolysis of 1,4-dihydro-5H-tetrazole derivatives (tetrazolines) generally results in the elimination of N_2. For instance, in inert solvents, 1,4-dimethyltetrazolinone (1a) yields dimethyldiaziridinone (2a);[1,2] the iminotetrazoline (3a) yields the iminodiaziridine (4a) and a minor amount of carbodiimide (5a);[1] and the thione derivatives (7a) and (7b) yield carbodiimides (8a) and (8b), respectively, together with sulphur.[1-3] There are numerous additional examples.[1-5] It is not certain whether loss of N_2 and formation of the final products is a concerted process in each of these reactions, or whether biradicals, e.g. (6), or zwitterions are involved as intermediates. When (3a) and (3b) were photolysed in butyronitrile matrices at 78 K, triplet tris(imino)methanes (6a) and (6b) were detected by e.s.r. spectroscopy.[6] These, however, might have been low-temperature by-products rather than intermediates in the formation of (4a) and (4b); and no such triplet species were detected after similar low-temperature photolysis of (1a) or (7a).

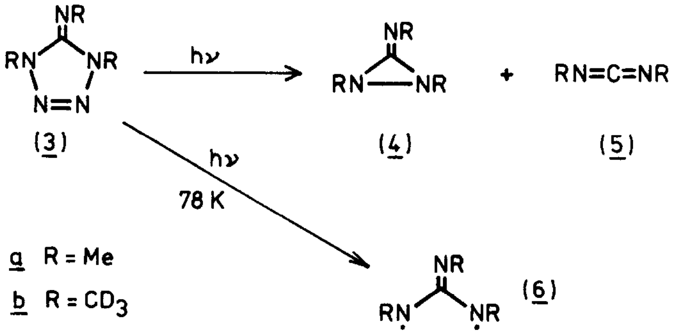
SCHEME 1.



(1) (2)

a R = Me, R' = Me
b R = Bu^t, R' = Pr^i

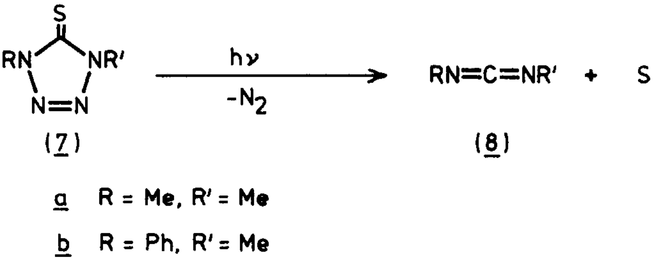
SCHEME 2.



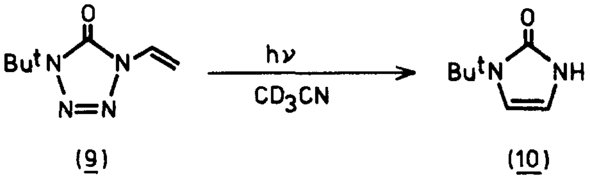
In the last few years, a number of 1-alkenyl-4-alkyltetrazolinones and -thiones have been synthesized and photolysed, to test the possibility that biradical or zwitterionic intermediates could be trapped by intramolecular [2+3]-cycloaddition to carbon-carbon double bonds.[7,8] In one such study, it was found that 254-nm photolysis of the 1-vinyltetrazolinone (9) in CD_3CN yielded 77% of imidazolone (10), a tautomer of the corresponding [2+3]-cycloadduct.[8] In MeOH, the yield of (10) was reduced to 45%, while cyclic and acyclic MeOH adducts were formed in competition. These results for (9) did indeed suggest that photoelimination of N_2 from tetrazolines proceeds via reactive acyclic intermediates, but the possibility of initial diaziridine formation in a concerted manner followed by photochemical rearrangement to (10) still could not be ruled out.

In view of the promising detection of (6a) and (6b) by e.s.r. spectroscopy at 78 K, it seemed worthwhile to carry out an ir. study of the photolysis of a series of tetrazolines isolated in inert matrices at 12 K. In this paper we report our results from the matrix photolysis of tetrazolinones (1a) and (9), iminotetrazolines (3a) and (3b), and tetrazolinethiones (7a) and (7b).

SCHEME 3.



SCHEME 4.



EXPERIMENTAL

Equipment.- The low-temperature cell has been described in detail previously.[9] It consisted of a CsBr or CsI window enclosed in a glass and metal vacuum shroud and cooled by an Air Products Displex (model CSA-202) closed-cycle He refrigerator. The base temperature was 12 K, and higher temperatures could be achieved by means of a small resistance heater connected to an Air Products APD-B temperature controller. Ir. spectra were recorded on a Perkin Elmer model 684 spectrometer interfaced with a Perkin Elmer 3600 Data Station. The spectrometer was calibrated regularly with a polystyrene film, and quoted frequencies have an estimated accuracy of ± 2 cm^{-1}. Photolysis was carried out with an Oriel 200 W high pressure Hg arc, which, in order to remove ir. radiation, was equipped with a water filter (13 cm pathlength) with quartz windows ($\lambda > 200$ nm).

Materials.- Research grade Ar (min. 99.9997%) and N_2 (min. 99.994%) were obtained from B.O.C. Ltd., and were used without further purification. 1,4-Dimethyl-1,4-dihydro-5H-tetrazol-5-one (1a),[2,10] 1,4-dimethyl-5-methylimino-1,4-dihydro-5H-tetrazole (3a) and its perdeuteriated analogue (3b),[1,6] 1,4-dimethyl-1,4-dihydro-5H-tetrazol-5-thione (7a),[2,11] 4-methyl-1-phenyl-1,4-dihydro-5H-tetrazol-5-thione (7b),[3] and 4-t-butyl-1-vinyl-1,4-dihydro-5H-tetrazol-5-one (9)[8] were all prepared as described previously.

Matrix deposition.- All the compounds studied were of relatively low volatility and were therefore sublimed directly on to the cold window at 20 K, with simultaneous deposition of a large excess of the host gas, the flow of which was controlled by a fine needle valve. Most of the compounds sublimed at a reasonable rate at room temperature; only compound (7b) required gentle warming to assist sublimation. The resulting matrices were cooled to 12 K after deposition. Matrix ratios (host/guest) could not be estimated. In some experiments deposition at 20 K and photolysis were carried out simultaneously. This technique has advantages which are discussed below.

RESULTS AND DISCUSSION

1,4-Dimethyl-1,4-dihydro-5H-tetrazol-5-one (1a).- Photolysis ($\lambda > 200$ nm) of tetrazolinone (1a) in Ar or N_2 matrices was very slow. In typical experiments, even 300 minutes irradiation removed less than half the starting-material. Reduction in the intensity of the ir. absorptions of (1a) [ν(C=O) 1745, 1739 cm^{-1} in Ar; 1743, 1733 cm^{-1} in N_2] was accompanied by the growth of new bands, the strongest of which was at 1895 cm^{-1} (both Ar and N_2 matrices) [Figure 1]. Diaziridinones with other than tertiary alkyl groups are known only in solution; so it was not possible to obtain a matrix spectrum of authentic dimethyldiaziridinone (2a). Nevertheless, the ir. spectrum of (2a) in CD_3CN at 233 K has been reported,[1,2] and in these conditions the ν(C=O) band was found at 1883 cm^{-1}. Also, the more stable diaziridinone (2b) has a ν(C=O) band at 1897 cm^{-1} in the gas phase, which is shifted to 1884 cm^{-1} in pentane solution.[2] We thus identify the

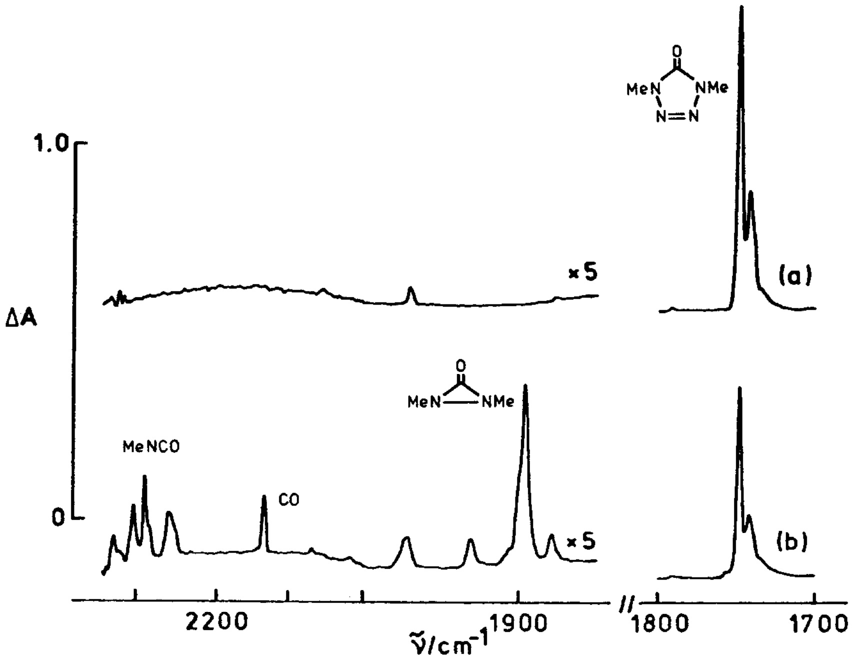
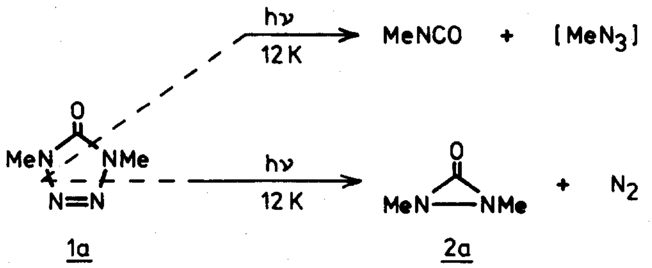


Figure 1. Ir. absorption spectra of (1a) in an Ar matrix at 12 K. (a) Before photolysis; (b) after 300 min λ >200 nm photolysis.

1895 cm^{-1} absorption in the matrix photoproduct spectrum of (1a) as belonging to dimethyldiaziridinone (2a). In addition to the bands of (2a), significant ir. absorptions at 2309, 2295, and 2263 cm^{-1} (Ar matrices) or at 2307, 2290, and 2258 cm^{-1} (N_2 matrices) also arose on photolysis of (1a) [Figure 1]. These occurred in the region characteristic of isocyanates[12] and are assigned to methyl isocyanate $\nu(NCO)_{as}$. Although there appears to be no report of a matrix ir. spectrum of MeNCO, $\nu(NCO)_{as}$ for the neat liquid occurs at 2288 cm^{-1}, with combination bands at 2318 and 2254 cm^{-1}; while the gas-phase spectrum shows several prominent features in the same region.[13] The formation of MeNCO in the matrix photolysis of (1a) was not the major pathway, since the $\nu(NCO)_{as}$ bands of isocyanates are always very strong, and yet that of MeNCO in Figure 1b is weaker than the $\nu(C{=}O)$ band of (2a). Nevertheless, this process has not been observed before in the solution photolysis of (1a), and represents a novel cleavage mode for (1a), in which C-N and N-N bonds are broken rather than two N-N bonds [Scheme 5]. The predicted second product of this cleavage, methyl azide, did not appear to survive the photolysis, which was not surprising in view of the long periods of irradiation needed to decompose appreciable amounts of (1a). It is of interest to note that, in the mass-spectrum of (1a), the base peak belongs to the molecular ion and the two most abundant fragments have m/z = 57 (56%) and 58 (68%), suggesting a similar fragmentation into isocyanate and azide species.[2]

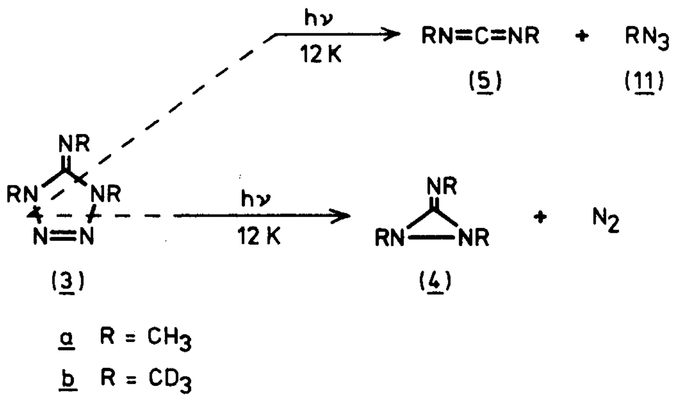
The only other photoproduct of (1a) that could be positively identified was some free CO (2138 cm^{-1} in Ar, 2140 cm^{-1} in N_2). This undoubtedly arose from secondary photolysis of either MeNCO or possibly diaziridinone (2a), but its formation was not examined further, owing to the very long photolysis times needed to produce reasonable quantities of the primary photoproducts.

SCHEME 5.



1,4-Dimethyl-5-methylimino-1,4-dihydro-5H-tetrazole (3a) and the perdeuteriated analogue (3b).-Matrix photolysis of the iminotetrazolines (3a) and (3b) produced similar reactions to those observed in solution [Scheme 6].[1] Photolysis of (3a) [ν(C=N) 1698, 1683 cm^{-1} in Ar; 1693, 1686 cm^{-1} in N$_2$] was accompanied by the growth of new ir. absorptions, the most significant of which are listed in Table 1. Amongst these were a group of five bands in the region 1875-1815 cm^{-1}. The iminodiaziridine (4a) in pentane solution exhibits a strong ν(C=N) absorption with ν_{max} at 1811 cm^{-1}, possessing at least three shoulders at higher frequencies up to about 1880 cm^{-1}; and related iminodiaziridines have similar strong absorptions in the same region.[14] We thus assign the 1875-1815 cm^{-1} bands in the photoproduct spectrum of (3a) to ν(C=N) of iminodiaziridine (4a). The splitting is probably due to Fermi resonance. The strongest product absorption, however, was a sharp unsplit band at 2153 (Ar) or 2150 cm^{-1} (N$_2$). This was assigned to dimethylcarbodiimide (5a), which has ν(NCN)$_{as}$ at 2168 and 2158 cm^{-1} in the gas phase, and at 2140 and 2152 cm^{-1} in the liquid and solid states, respectively.[15] The carbodiimide was probably formed in the alternative [2+3]-cycloelimination shown in Scheme 6, and should have been accompanied by methyl azide (11a). As noted above, methyl azide is very photolabile, and was unlikely to survive the photolysis conditions of our experiments. Nevertheless, a weak band at 2100 cm^{-1} (N$_2$) was observed in one of the experiments, and this was tentatively assigned to ν(NNN)$_{as}$ of methyl azide. Support for this assignment came from an experiment in which photolysis of (3a) was carried out simultaneously with matrix deposition. In these conditions, primary photoproducts are protected to a certain extent by successive layers of the matrix gas-mixture acting as a light filter for those already deposited.[16] With (3a) it was found that the 2100 cm^{-1} product band was much more prominent after simultaneous photolysis and deposition than in more conventional experiments.

SCHEME 6.



The primary photoproducts (4a) and (5a) were resistant to further photolysis ($\lambda > 200$ nm), and the matrix product ir. spectra showed little change on continued irradiation of the matrices. Moreover, annealing matrices containing the photoproducts of (3a) to 35 K did not change the ir. spectra either. Thus there was no evidence for the presence of triplet biradical (6a) among the primary photoproducts, since this species would be expected to be quite reactive and undergo cyclization to (4a) or other secondary thermal or photochemical processes.

Photolysis of the perdeuteriated iminotetrazoline (3b) in Ar and N_2 matrices proceeded in an exactly analogous manner. The product ir. spectra (Table 1) showed the presence of both the iminodiaziridine (4b) and the carbodiimide (5b). Trideuteriomethyl azide (11b), however, was not detected in these experiments. As with (3a), annealing matrices after photolysis of (3b) caused no alteration in the ir. spectra, again suggesting that a biradical, (6b) in this case, was not present in significant amounts.

TABLE 1. Ir. bands (cm^{-1}) observed after matrix photolysis ($\lambda > 200$ nm) of iminotetrazolines (3a) and (3b).

	in N_2	in Ar	Assignment	Species
Precursor (3a)	1693 s†	1698 s	ν(C=N)	(3a)
	1686 s	1683 s	"	"
Products	2150 s	2153 s	$\nu(N{=}C{=}N)_{as}$	(5a)
	2100		$\nu(N_3)_{as}$	(11a)
	1884	1886	ν(C=N)	(4a)
	1870 m	1872	"	"
	1842 m	1841 m	"	"
	1824 m	1826	"	"
	1816 m	1817 m	"	"
Precursor (3b)	1681 s	1696	ν(C=N)	(3b)
		1688 s	"	"
		1679 s	"	"
Products	2148 s	2152 s	$\nu(N{=}C{=}N)_{as}$	(5b)
	1838 s	1835 s	ν(C=N)	(4b)
	1833 s	1825	"	"

†Bands were weak unless denoted s (strong) or m (medium)

1,4-Dimethyl-1,4-dihydro-5H-tetrazol-5-thione (7a) and 1-phenyl-4-methyl-1,4-dihydro-5H-tetrazol-5-thione (7b).- The two thiones (7a) and (7b) were photolysed only very slowly in N_2 matrices ($\lambda > 200$ nm), and appeared to give only the corresponding carbodiimides (8a) [$\nu(NCN)_{as}$ 2150 cm^{-1}] and (8b) [$\nu(NCN)_{as}$ 2150 and 2140 cm^{-1}]. No evidence for an alternative fragmentation into an isothiocyanate [$\nu(NCS)_{as}$ 2110-2050 cm^{-1}][11] and an azide was found for either of the thiones, nor was there any indication of other reactive species amongst the photoproducts. The matrix photolysis of (7a) and (7b), therefore, appears to proceed exactly as in solution at higher temperatures.

4-t-Butyl-1-vinyl-1,4-dihydro-5H-tetrazol-5-one (9).- The matrix photochemistry of (9) was found to be both complex and interesting. The primary products arise in two different fragmentations and undergo further photochemical decomposition. Matrix photolysis ($\lambda > 200$ nm) of (9) led to fairly rapid decomposition, and in the early stages new ir. bands arose at 2310-2260 cm^{-1}

[isocyanate $\nu(NCO)_{as}$], at 2125-2090 cm^{-1} [azide $\nu(NNN)_{as}$], at 1950-1860 cm^{-1} [diaziridinone $\nu(C=O)$ and Fermi resonance], and at 1635 cm^{-1} [vinyl $\nu(C=C)$] [Table 2 and Figure 2]. Thus both N_2 elimination and isocyanate-azide fragmentation take place [Scheme 7]. The yield of the most photolabile product, vinyl azide (13), could be much increased by simultaneous deposition and irradiation (see above)[Figure 3].

TABLE 2. Ir. bands (cm^{-1})
observed after matrix photolysis ($\lambda > 200$ nm) of tetrazolinone (9).

	in N_2	in Ar	Assignment	Species
Precursor (9)	1740 s†	1742 s	$\nu(C=O)$	(9)
	1735 s	1735 s	"	"
	1655 m	1658 m	$\nu(C=C)$	"
	1644 m	1646 m	"	"
Primary products	2305	2309	$\nu(N=C=O)_{as}$	(12)
	2280	2282	"	"
	2260 s	2260 s	"	"
	2123		$\nu(N_3)_{as}$	(13)
	2092	2093	"	"
	1946		$\nu(C=O)$	(15)
	1914	1912	"	"
	1889		"	"
	1864 m	1864 m	"	"
	1634	1633	$\nu(C=C)$	"
Secondary products	2140	2138	$\nu(CO)$	CO
	2045	2042	$\nu(C=C=N)_{as}$	(16)
	1669	1671	$\nu(C=N)$	(14)

†Bands were weak unless denoted s (strong) or m (medium)

Two of the primary photoproducts were photolabile. On continued irradiation ($\lambda > 200$ nm), bands due to diaziridinone (15) and vinyl azide (13) decreased in intensity, but the $\nu(NCO)_{as}$ absorption of t-butyl isocyanate (12) increased further. The increase in the isocyanate was much greater at this stage than could be attributed solely to loss of the remaining tetrazolinone (9) [Figure 2]; so that a second route to the isocyanate via diaziridinone (15) was implicated [Scheme 7]. It should be emphasized, however, that the presence of vinyl azide (13) amongst the products demonstrated that not all the isocyanate derived from the diaziridinone. While these intensity changes in the ir. absorptions of (12), (13) and (15) were taking place, new bands arose at 2138, 2042, and 1671 cm^{-1} (Ar) or 2140, 2045, and 1669 cm^{-1} (N_2). These were assigned to free CO, ketenimine (16), and imine (14), respectively. Ketenimine (16), the expected photolysis product of vinyl azide, has previously been found to have a very strong $\nu(CCN)_{as}$ band at 2040 cm^{-1} in Ar matrices,[17] and the bands at 2042(Ar) or 2045 cm^{-1} (N_2) belonging to one of the secondary products in the matrix photolysis of (9), are in good agreement with the previous report and are thus assigned to (16). In each matrix, the $\nu(CCN)_{as}$ band of (16) grew at approximately the same rate as that at which the $\nu(NNN)_{as}$ band of vinyl azide diminished. The secondary product bands at about 1670 cm^{-1} are assigned to $\nu(C=N)$ of the imine (14), for which a matrix ir. spectrum has also already been reported.[18] The growth in the imine absorption did not appear connected with the diminution of the azide absorptions, but followed the growth in CO quite closely. Hence imine (14) could have arisen either by secondary photolysis of t-butyl isocyanate, or by an alternative decomposition pathway of excited state (15). Authentic t-butyl isocyanate did not undergo any detectable decomposition when irradiated under the conditions of our experiments in Ar or N_2 matrices; so that imine (14) most probably arose by the latter route [Scheme 7].

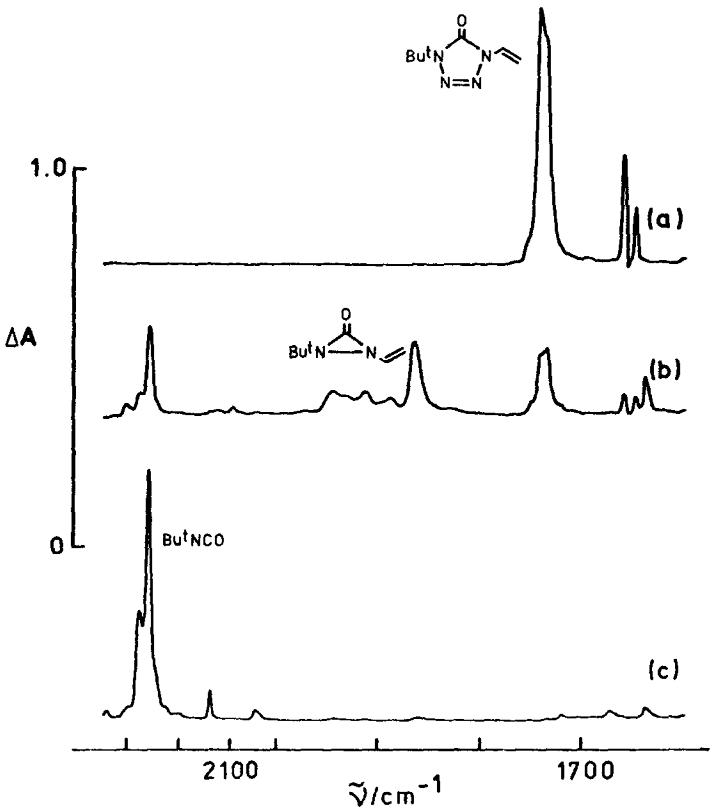
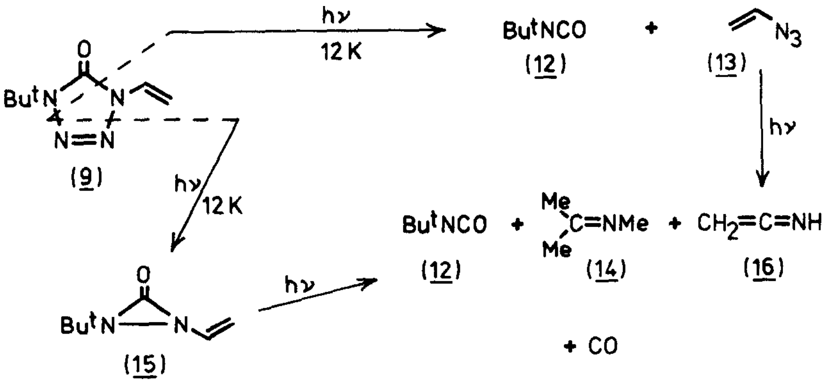


Figure 2. Ir. absorption spectra of (9) in an N_2 matrix at 12 K. (a) Before photolysis; (b) after 15 min λ > 200 nm photolysis; (c) after 300 min λ > 200 nm photolysis.

SCHEME 7.



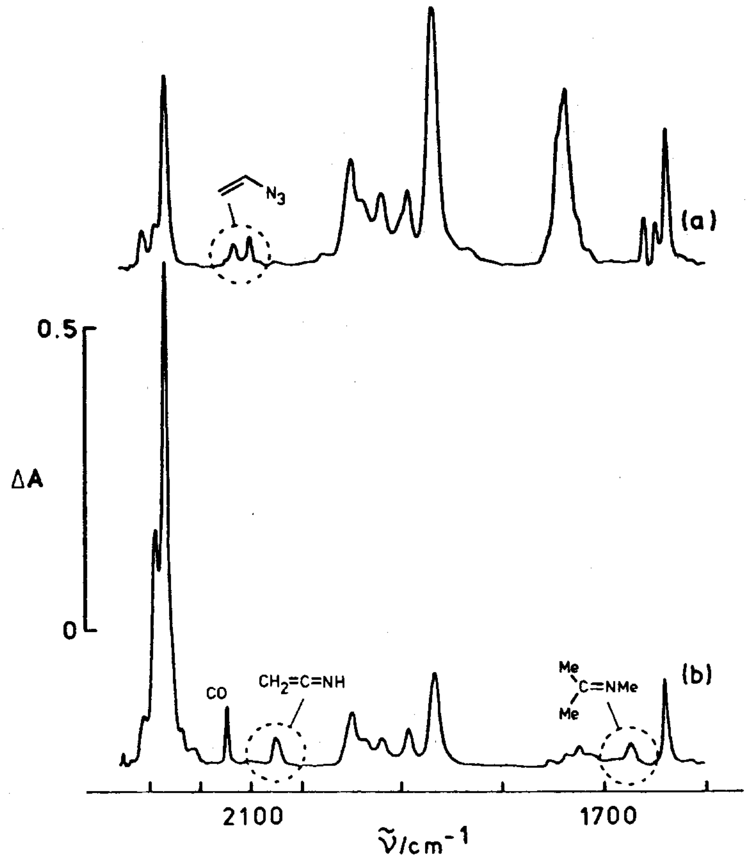


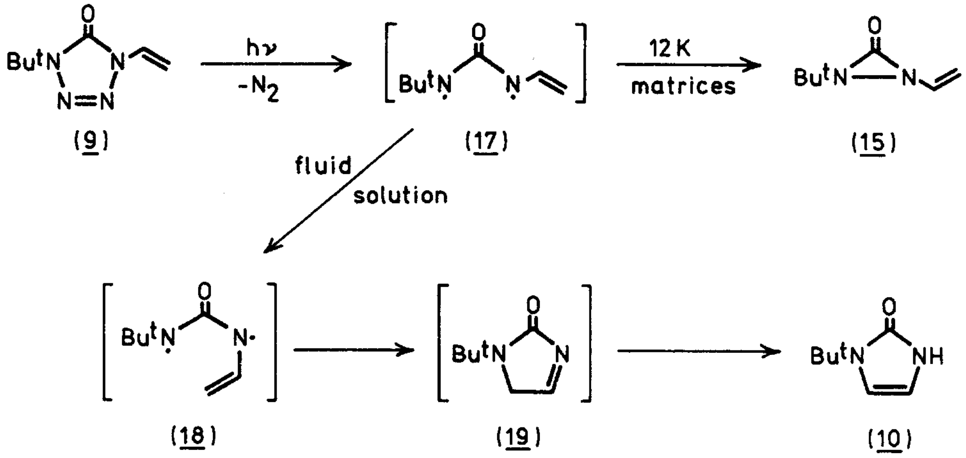
Figure 3. Ir. absorption spectra of (9) and its photoproducts in an N_2 matrix at 12 K. (a) After deposition with continous λ>200 nm irradiation; (b) after a further 150 min λ>200 nm irradiation.

CONCLUSIONS

Photolysis of dimethyltetrazolinone (1a) in low-temperature Ar and N_2 matrices proceeds in a similar manner to the solution photolysis at ambient temperatures, yielding dimethyldiaziridinone (2a) as the major product. In the matrices, however, a second minor reaction pathway is also followed, which leads to MeNCO and presumably methyl azide [Scheme 5]. The iminotetrazolines (3a) and (3b) give the corresponding carbodiimides (5a) and (5b), and iminodiaziridines (4a) and (4b), when photolysed either in solution at ambient temperatures or in matrices; and the tetrazoline thiones (7a) and (7b) give carbodiimides (8a) and (8b), respectively, under both sets of conditions. For all these compounds, therefore, matrix photolysis proceeds in much the same way as solution photolysis, the only exception being the minor cleavage pathway of (1a), which appears to occur only in low-temperature matrices. In none of these cases were any biradical or other reactive intermediates detected in the matrix ir. experiments, although biradicals (6a) and (6b) have previously been detected by e.s.r.^{6}

4-*t*-Butyl-1-vinyl-tetrazolinone (9) is exceptional: its photolysis in low-temperature matrices gives a completely different set of products from those obtained in solution at ambient temperatures. In the inert solvent CD_3CN, the photoproduct is the imidazolone (10), but the yield of this is reduced in MeOH, and acyclic MeOH adducts are produced as well.^{8} In low-temperature matrices, however, photolysis of (9) gives *t*-butyl isocyanate (12), vinyl azide (13), and the diaziridinone (15) as primary products, and imine (14) and ketenimine (16) as secondary products. *t*-Butyl isocyanate is also produced in an alternative route by secondary photolysis of (15) [Scheme 7]. The isocyanate-azide fragmentation pathway is similar to that observed in the matrix photolysis of (1a), and its enhancement from negligible importance at ambient temperatures to a reasonably competitive reaction channel at low-temperatures is presumably either a temperature or a medium effect, which operates at least for the two tetrazolinones studied so far, and possibly more generally. The formation of the diaziridinone (15) in the matrix photolysis of (9) is very interesting, because this product is not found at all in the solution photochemistry. The divergence of results from the two sets of experiments can be rationalized very satisfactorily, however [Scheme 8]. Initial elimination of N_2 from (9) will give the biradical (17) in a transoid conformation. If, as seems likely, the low-temperature matrices provide a rigid environment which prevents biradical (17) from undergoing any conformational change, ring closure to the diaziridinone (15) becomes the only feasible reaction. In a fluid solvent, on the other hand, bond rotation will not be hindered by the medium, and the cisoid conformation (18) of the biradical will be accessible. Ring closure of (18), which can also be regarded as an intramolecular [2+3]-cycloaddition, will yield (19), and ultimately the tautomer (10) which was actually isolated. The matrix photolysis of (9), therefore, provides additional evidence for the intermediacy of biradicals in the photolysis of tetrazolines, even though no biradical was detected directly by ir. spectroscopy in these matrix experiments.

SCHEME 8.



References

1. H.Quast and L.Bieber, Angew.Chem. (1975) 87, 422; Angew.Chem.Int.Ed.Engl. (1975) 14, 428.
2. H.Quast and L.Bieber, Chem.Ber. (1981) 114, 3253.
3. H.Quast and U.Nahr, Chem.Ber. (1985) 118, 526.
4. H.Quast, Heterocycles (1980) 14, 1677.
5. H.Quast, A.Fuss, and U.Nahr, Chem.Ber. (1985) 118, 2164.
6. H.Quast, L.Bieber, and W.C.Danen, J.Amer.Chem.Soc. (1978) 100, 1306.
7. H.Quast and U.Nahr, Chem.Ber. (1983) 116, 3427.
8. H.Quast and U.Nahr, Chem.Ber. (1984) 117, 2761.
9. I.R.Dunkin and J.G.MacDonald, J.Chem.Soc., Perkin Trans.2 (1984) 2079. J.G.MacDonald, Ph.D. Thesis, University of Strathclyde, Glasgow (1980).
10. S.Hünig and K.H.Oette, Justus Liebigs Ann.Chem. (1961) 641, 94.
11. W.Tochtermann, H.Gustmann, and C.Wolff, Chem.Ber. (1978) 111, 566.
12. L.J.Bellamy, "Advances in Infrared Group Frequencies," Chapman and Hall, London (1968) vol.2.
13. R.P.Hirschmann, R.N.Knisely, and V.A.Fassel, Spectrochim.Acta (1965) 21, 2125.
14. K.-H.Ross, Dissertation, Universität Würzburg (1974).
15. G.Papi and G.Sbrana, J.Amer.Chem.Soc. (1971) 93, 5213.
16. C.J.Shields, Ph.D. Thesis, University of Strathclyde, Glasgow (1985).
17. M.E.Jacox and D.E.Milligan, J.Amer.Chem.Soc. (1963) 85, 278. M.E.Jacox, Chem.Phys. (1979) 43, 157.
18. I.R.Dunkin and P.C.P.Thomson, Tetrahedron Lett. (1980) 21, 3813.