

PHOTOCHEMICAL FRAGMENTATION OF MESOTONIC 1,3,4-THIADIAZOLES: A MECHANISTIC OBSERVATION

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Abstract—Photochemistry, synthesis, nucleophilic addition photoreaction, low temperature photolysis, and quantum yield calculations of representative members have been studied in understanding the mechanism of the photofragmentation of mesoionic 1,3,4-thiadiazoles. Quantum yield calculations suggest self quenching and unimolecularity in the ring opening reaction while timed interval IR recording shows the formation of heterocumulenes during photolysis.

Photochemical oxidative cyclisation of mesoionic 4,5-diaryl 1,3,4-thiadiazoles, -oxazoles, -thiazoles and -imidazoles at 3000 Å in protic solvents in presence of oxygen or any other oxidising agent to phenanthro heterocyclic systems has been known^{1,2} for quite some time. However, for N-4 or C-5 alkyl substituted mesoionic 1,3,4-thiadiazoles of type (1a-c), the photochemically induced oxidative cyclisation is clearly unlikely. Naturally in continuation of the study^{1,3,4} on the photochemistry of mesoionic systems, we have investigated the photolysis of compounds 1a-e and found a new mode of photofragmentation as well as an interesting wavelength dependence for the course of the reaction which is the subject of this communication.

The thiadiazoles 1a, 1c and 1d-e were prepared by known methods⁵⁻⁷ and 1b was obtained in quantitative yield upon condensing carbon disulphide with N-thiobenzoyl-N-methylhydrazine (2)^{8,9} in presence of pyridine and thus the hazards of thiophosgene¹⁰ was avoided.

Irradiation of 1a-e in 0.01M acetonitrile at 2537 Å for 72 hr at room temperature in nitrogen atmosphere with low pressure mercury lamp using quartz filter yielded the thioamides (3a-d) and elemental sulphur [e.g. 1a → 20% N-phenylthioacetamide (3a),¹¹ m.p. 76° and 35% sulphur; 1b → 21% N-methylthiobenzamide 3b,¹² m.p. 79° and 40% sulphur; 1c → 25% N-methylthiobenzamide 3b,¹² m.p. 79°; 1d¹³ → 27% N-phenylthiobenzamide 3c,¹⁴ m.p. 101° and 25% sulphur; and 1e → 20% N-phenyl-p-methoxy thiobenzamide 3d,¹⁵ m.p. 155° and 30% sulphur].

As a working hypothesis for the explanation of the photofragmentation reactions of mesoionic 1,3,4-thiadiazoles we propose an initial valence tautomerisation to yield N-isothiocyanatothioamide (4)† which undergoes homolytic fission of the N-N bonds to yield the radical

precursor of the thioamide and the isothiocyanate radical. The thioamide is formed by hydrogen abstraction from solvent.^{3,17} When the photolysis of 1b was repeated in acetonitrile and methanol mixture (4:1), a yield of 35% N-methylthiobenzamide (3b) was obtained with 26% sulphur: thus the yield of the thioamide increases in 1b to 3b with the better hydrogen donor solvent methanol. The photochemical decomposition of the isothiocyanate group is known to proceed with the loss of elemental sulphur.^{18a} §

In order to substantiate this reaction pathway, photolysis of 1b was carried out in acetonitrile and n-butylamine mixture (1:1) at 2537 Å with a view to intercept the postulated intermediate (4). A 52% yield of N-methylthiobenzamide (3b) was obtained and significantly no sulphur was produced. We interpret this to mean that nucleophilic addition of the n-butylamine has occurred at the open chain stage (5) and subsequent decomposition of 6 proceeds as indicated.¶ In this second stage photolysis only 3b was formed although n-butylthiourea (7) could also be a product. For further proof of this photoreaction pathway, it was necessary to synthesise both 6 and 7 and photolyse them under similar conditions. During the photodecomposition of 6 heavy evolution of hydrogen sulphide was observed which was trapped by silver nitrate.

Compound 6, m.p. 69–70°, synthesised by the condensation of n-butylthioisocyanate with N-thiobenzoyl-N-methylhydrazine (2) was photolysed at 2537 Å in acetonitrile. Heavy evolution of hydrogen sulphide was observed besides formation of 46% of 3b. Finally n-butylthiourea (7), m.p. 78°, prepared by bubbling dry ammonia gas into a benzene solution of n-butylthioisocyanate following the method of Hoffmann¹⁹ upon photolysis and working up gave the unreacted material back in quantity.

Further attempt to elucidating the mechanism of the photoisomerisation of mesoionic 1,3,4-thiadiazoles, low temperature synthesis of 1b by condensing dicyclohexyl carbodiimide²⁰ with 2 with a view to trapping the intermediate (5) was tried. But in every instance cyclisation took place giving 1b and 1,3-dicyclohexyl thiourea²¹ as the bye product.

Finally intermediacy of the N-isothiocyanatothioamide (5) has been demonstrated by timed interval IR recording during the course of photolysis at variable temperatures.^{22,23} Photolyses were carried out in nujol mull, neat melt, and in acetonitrile solution and the development of

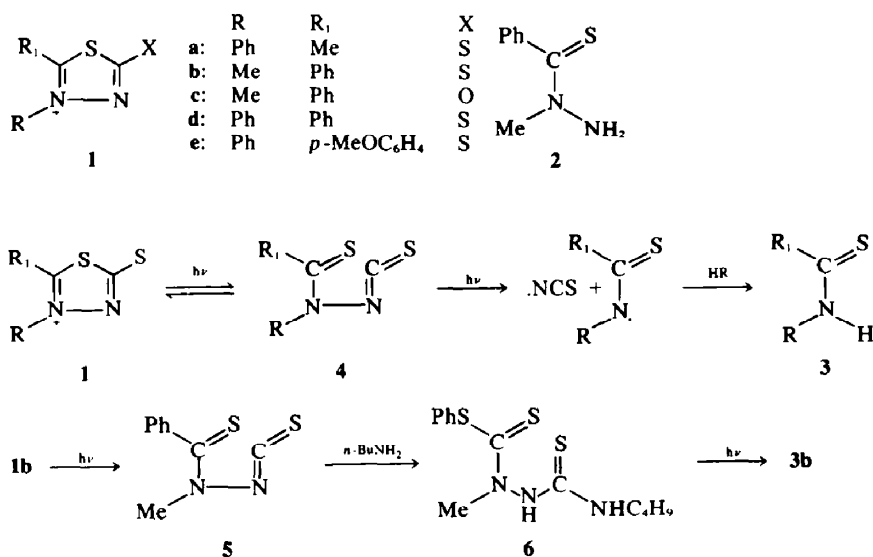
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†Such valence tautomerisation occurs in the case of analogous 1,3,4-thiadiazol 2-olates.

^{16a} The occurrence of a carbonyl band at 1630–1650 cm⁻¹ indicates the semicyclic nature of these compounds.^{16b}

§The behaviour of the isothiocyanate radical under photolytic conditions has been investigated and the reaction (NCS)₂ → 2NCS reported.^{18b}

¶In a dark experiment the stability of 1b towards n-butylamine under reaction conditions was established.



absorption in the heterocumylene region of the spectra was observed.

Figure 1(a) shows the appearance of the $-N=C=S$ absorption at 2060 cm^{-1} for 4-methyl 5-phenyl 1,3,4-thiadiazolium 2-thiolate (**1b**) at 25° after photolysis of 3 hr in a acetonitrile solution.^{23,24} Similarly, absorption at 2060 cm^{-1} developed upon irradiation of **1b** in nujol or neat melt. Analogous behaviour was found for 4-phenyl 5-methyl 1,3,4-thiadiazolium 2-thiolate (**1a**).

That there is both a thermal component in the photochemical ring opening and a dark thermal pathway is indicated by two observations; (a) irradiation of **1b** at -190° for 4 hr caused no development of $-N=C=S$ absorption; (b) heating of **1a** at 160° with simultaneous recording of the IR spectrum leads to strong absorption at 2060 cm^{-1} .

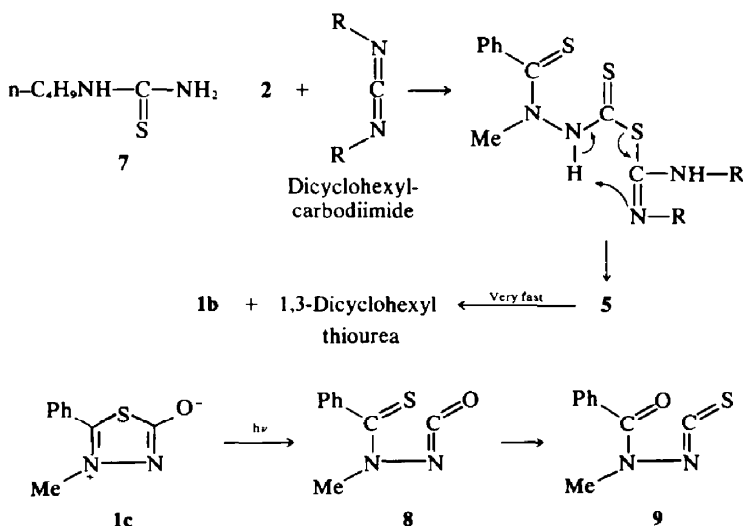
Photolysis of 4-methyl 5-phenyl 1,3,4-thiadiazolium 2-olate (**1c**) at 25° in acetonitrile solution or as nujol mull caused development of absorption at 2260 cm^{-1} ($-N=C=O$),²⁵ in agreement with Scheme 1. Figure 1(b) illustrates this behaviour.

The unexpected reaction (**8**→**9**) was observed in the

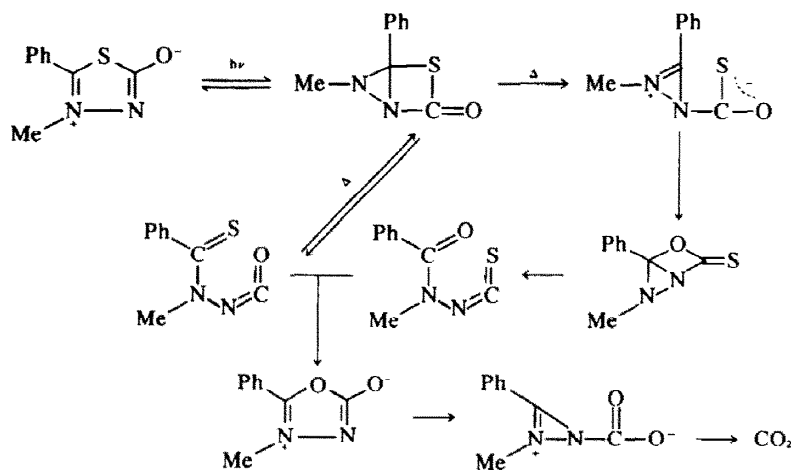
photolysis of **1c** in both Nujol mull and acetonitrile solution by the gradual disappearance of absorption at 2060 cm^{-1} ($-N=C=S$). In the solution photolysis the initial $-N=C=O$ band increases in intensity. This conversion may be due to either bimolecular reaction or a unimolecular isomerisation. Erner²⁶ has shown that isocyanates and isothiocyanates undergo an exchange reaction presumably via ring complexes formation when heated together. This rearrangement is akin to thionothio rearrangements which are well known.

The absorption which appears at 2350 cm^{-1} may be due to CO_2 formed by photofragmentation as depicted in Scheme 2.²⁷

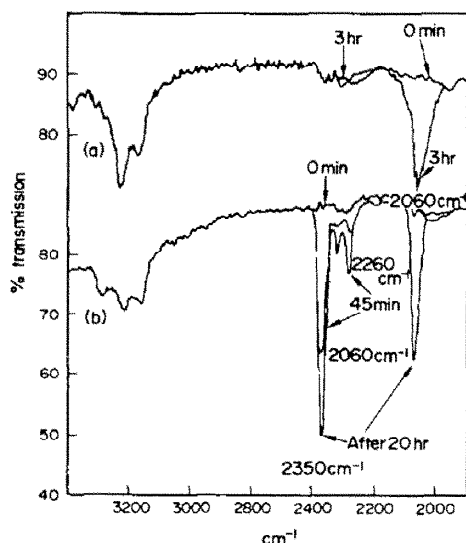
The quantum yields for the disappearance of two typical members, 4-methyl 5-phenyl 1,3,4-thiadiazolium 2-thiolate (**1b**) and 4-methyl 5-phenyl 1,3,4-thiadiazolium 2-olate (**1c**) are shown in the Table 1. The ϕ_{dis} of **1b** and **1c** were measured by the reduction of 385 and 320 nm peaks, respectively. The absence of reaction ($\phi_{dis} = 0.00$) for **1c** at 10^{-2} M concentration suggests self-quenching and implies that the initial ring-opening reaction is unimolecular.



Scheme 1.



Scheme 2.



acetonitrile in light yellow needles (80%), m.p. 219° (lit.^{6,13} m.ps. 219–221°, 216°), M^+ 208, λ_{max} (MeOH) 262 and 350 nm (log ϵ 4.08 and 3.51), (MeCN) 266 and 365 nm (log ϵ 4.07 and 3.48); 1c, crystallised from acetonitrile in colourless thick rods (90%), m.p. 176° (lit.⁷ m.p. 178–179°), M^+ 192, λ_{max} (MeOH) 233 and 311 nm (log ϵ 3.89 and 3.91), (MeCN) 234 and 320 nm (log ϵ 3.99 and 3.87); 1d, crystallised from acetonitrile in orange needles (35%), m.p. 227° (lit.^{6,13} m.ps. 228–229°, 222–223°), M^+ 270, λ_{max} (MeOH) 281 and 398 nm (log ϵ 4.26 and 3.72), (MeCN) 276 and 410 nm (log ϵ 4.29 and 3.74); and 1e, crystallised from CHCl_3 and EtOH mixture in orange needles (35%), m.p. 236° (lit.⁶ m.p. 228–229°), M^+ 300, λ_{max} (MeOH) 280 and 395 nm (log ϵ 4.01 and 3.96), (MeCN) 286 and 408 nm (log ϵ 4.24 and 3.85).

Compound **1b** was prepared by dissolving **2**, m.p. 91–92° (lit.⁹ m.p. 92°), IR 3220 and 3100 (NH₂) and 1370 (C=S), δ 6.32 (s, 5H, ArH), 5.59 (b, 2H, NH₂) and 3.25 (s, 3H, N-Me), 3.3 g in CS₂ and refluxing the soln for about 0.5 hr with a few drops of dry pyridine. Removal of excess of CS₂ and pyridine followed by recrystallisation furnished **1b** (4.1 g, 98%) in yellow needles, m.p. 229° (lit.¹⁰ m.p. 221°), M⁺ 208, λ_{max} (MeOH) 265 and 380 nm (log ϵ 4.16 and 3.86), (MeCN) 271 and 385 nm (log ϵ 4.09 and 3.76).

Compound	Concentration ^a	ϕ_{dis}
1b	10^{-3} M	0.04
1c	10^{-3} M	0.002
1c	10^{-2} M	0.00

^a In acetonitrile solution.

EXPERIMENTAL

M.ps were taken in capillary tubes in a Thomas-Hoover m.p. apparatus and are uncorrected. Micro analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL 60076, U.S.A. IR spectra were measured in a Perkin-Elmer 521 spectrophotometer in Nujol and the UV spectra were run in a Cary 14 machine. NMR spectra were recorded on a Varian A60 spectrometer in CDCl₃, using TMS as the internal standard and the mass spectra were measured in an AEI MS-9 spectrometer operating at 70 eV.

Materials. The mesoionic 1,3,4-thiadiazoles were prepared according to the procedures outlined^{4,7} [**1a**, crystallised from

Typical irradiation experiments with Rayonet 2537 Å lamps with quartz filter. Degassed solns (500 ml), 0.01 M of 1a-e in acetonitrile were irradiated in a Quartz vessel under N₂ for an extended period of time, 72 hr. Removal of the solvent and chromatographic resolution on silica gel furnished the thioamides [1a (1.04 g) gave 3a, crystallised from benzene-hexane mixture in needles (150 mg, 20%), m.p. 76° (lit.¹¹ m.p. 76°), M⁺ 151, IR 3200 (NH) and 1370 (C=S), λ_{max} (MeOH) 217 and 297 nm (log ε 4.13 and 4.10), (MeCN) 219 and 296 nm (log ε 4.20 and 4.09), 810-50 (b, 1H, NH), 7.68 (m, 2H, ArH), 7.26 (m, 3H, ArH), and 2.57 (d, J 10 Hz, 3H, C.Me) and elemental sulphur, m.p. 114-115° (35%); 1b (1.04 g) gave 3b (158 mg, 21%), crystallised from benzene and hexane in needles, m.p. 78-79° (lit.¹² m.p. 79°), M⁺ 151, IR 3300 (NH) and 1380 (C=S), λ_{max} (MeOH) 239 and 286 nm (log ε 4.03 and 3.88), (MeCN) 240 and 287 nm (log ε 3.96 and 3.78), 8.8-13 (b, 1H, NH), 7.60 (m, 2H, ArH), 7.27 (m, 3H, ArH), and 3.17 (d, J 6 Hz, 3H, N.Me) and sulphur (40%); 1c (0.96 g) gave 3b (189 mg, 25%), m.p. 79° (lit.¹² m.p. 79°), M⁺ 151; 1d, (1.35 g) gave 3c (288 mg, 27%), crystallised from benzene in yellow needles, m.p. 101° (lit.¹⁴ m.p. 102°), M⁺ 213, IR 3300 (NH) and 2375 (C=S), λ_{max} (MeOH) 236, 266 and 314 nm (log ε 4.22, 4.13 and 3.93), (MeCN) 238, 266 and 326 nm (log ε 4.21, 4.12 and 3.93), 8.9-11 (b, 1H, NH), 7.70 (m, 4H, ArH), and 7.30 (m, 6H, ArH) and sulphur (35%); and 1e (1.5 g) gave 3d (243 mg, 20%), crystallised from benzene in yellow needles, m.p. 155° (lit.¹⁵ m.p. 153-154°), M⁺ 243, IR 3320 (NH) and 1370 (C=S), λ_{max} (MeOH) 222 and 290 nm (log ε 4.29 and 4.29), (MeCN) 225 and 292 nm (log ε 4.33 and 4.33), 8.11-00 (b, 1H, NH), 7.80 (d, J 9 Hz, 2H, A₂B₂, ArH), 7.67 (m, 2H, ArH), 7.30 (m, 3H, ArH), 6.80 (d, J 9 Hz, 2H, A₂B₂, ArH), and 3.69 (s, 3H, O.Me) and sulphur (30%)].

Photolysis of 1b in presence of methanol. Irradiation of 1b in MeCN and MeOH mixture (4:1), 500 ml, (0.01 M), in the same way as before and working up gave 3b (264 mg, 35%), crystallised from benzene and hexane in needles, m.p. 79° (lit.¹² m.p. 79°) and sulphur (26%).

Irradiation of 1b in n-butylamine. Irradiation of 1b in MeCN and n-BuNH₂ mixture (1:1), 500 ml, (0.01 M), in the usual way evolved H₂S which was trapped by AgNO₃. The reaction after removal of solvent and chromatography gave 3b (394 mg, 52%), crystallised from benzene and hexane in needles, m.p. 79° (lit.¹² m.p. 79°).

Synthesis of the intermediate 6. To a soln of 2 (1.66 g, 0.01 mol) in 30 ml dry benzene, n-butylthiocyanate (1.15 g, 0.01 mol) was added dropwise while the reaction was stirred vigorously. After complete addition the reaction was refluxed for 2 hr, cooled, freed from solvent and excess n-butylthiocyanate and chromatographed over silica gel when pure 6 was obtained (2.1 g, 75%), which was finally crystallised from benzene and hexane in flakes, m.p. 69–70°, IR 3220 (NH) and 1380 (C=S), λ_{max} (MeOH) 240 and 280 nm (log ϵ 4.32 and 3.98), (MeCN) 243 and 285 nm (log ϵ 4.29 and 3.87), δ 7.30 (s, 5H, ArH), 6.13 (b, 2H, NH), 3.43 (bm, 2H, CH₂), 3.29 (s, 3H, N.Me), 1.44 (bm, 4H CH₂) and 0.93 (t, 3H, C.CH₃) (Found: C, 55.76; H, 6.66; N, 15.01; S, 22.90. C₁₁H₁₉N₃S₂ requires: C, 55.51; H, 6.76; N, 14.93; S, 22.78%).

Irradiation of the intermediate 6. Soln of 6 in MeCN (1.405 g, 500 ml, 0.01 M) was irradiated in the same way as before when copious evolution of H₂S was noticed which was trapped by AgNO₃. The reaction upon working up in the usual way furnished 3b (347 mg, 46%), crystallised from benzene and hexane mixture in needles, m.p. 79° (lit.¹² m.p. 79°).

Preparation of n-butylthiourea (7). To an ice cold soln of n-butylthiocyanate (2.3 g, 0.02 mol) in dry benzene (30 ml), dry ammonia gas was bubbled through for 4 hr when the whole reaction became colourless solid. Compound 7 thus obtained in quantitative yield was crystallised from chloroform and acetonitrile mixture in needles, m.p. 78° (lit.¹⁹ m.p. 79°), IR 3300 (NH) and 1380 (C=S).

Photolysis of the thiourea (7). Irradiation of 0.01 M acetonitrile soln of 7 (0.66 g, 500 ml) in the usual manner followed by working up gave 7 back in quantity (0.66 g), crystallised from chloroform and acetonitrile mixture in needles, m.p. 78° (lit.¹⁹ m.p. 79°).

Attempted synthesis of 1b by carbodiimide reaction. In an ice cold soln of 2 (0.83 g, 0.005 mol) in 3 ml CS₂, soln of carbodiimide (1.03 g, 0.005 mol) in 2 ml CS₂ was added dropwise with stirring. After complete addition the reaction was left over night at room temp. The yellow solid showed three spots on TLC corresponding to 1b, 1,3-dicyclohexyl thiourea, and 2 with a ghost spot for carbodiimide. The solid after washing with ether gave pure 1b (364 mg, 35%), m.p. 227° (lit.¹⁰ m.p. 221°) while the mother liquor upon separation by TLC gave unreacted 2 (210 mg, 25%), m.p. 92° (lit.^{8,9} m.p. 92°), and 1,3-dicyclohexyl thiourea (300 mg, 25%), m.p. 179–180° (lit.²² m.p. 180–181°); IR 3250 (NH) and 1375 (C=S), m.m.p. 179–180° (authentic sample kindly provided by Dr. J. De Jong).

Repetition of the carbodiimide reaction at room temp with same starting materials in the same molar ratios as before, keeping overnight, after working up gave pure 1b (580 mg, 56%), m.p. 228° (lit.¹⁰ m.p. 221°) and 1,3-dicyclohexyl thiourea (320 mg, 28%), m.p. 180° (lit.²¹ m.p. 180–181°), m.m.p. 180°.

Variable temperature irradiation of 1a–c. Variable temp irradiation of 1a–c in Nujol mull, neat melt, and in acetonitrile soln with timed interval IR recordings were carried out according to the procedures outlined by Chapman *et al.*²² and Eckroth and Squire.²³ As the light source, an 800 W lamp with maximum emission at 3660 Å was used.

Quantum yields. Experiments for the quantum yield calculations for 1b and 1c were performed following the procedures described by Eckroth and Squire²⁴ by the reduction of 385 and 320 nm peaks, respectively. Calculations of quantum yield were done according to the procedures described by Calvert and Pitts.²⁸

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