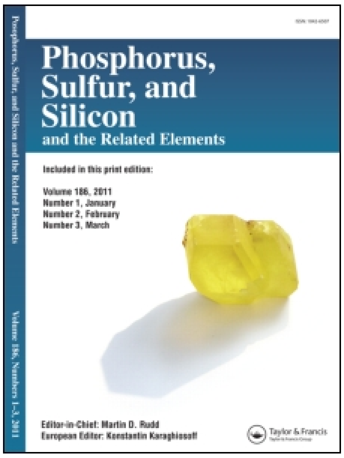


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE PHOTOLYSIS OF 1,3,4-THIADIAZOLIDINE-2,5-DITHIONES IN PRESENCE AND IN ABSENCE OF SINGLET OXYGEN

M. F. Zayed[a]; T. S. Hafez[a]; N. Khir El-din[a]; E. Hefny[a]
[a] National Research Centre, Dokki, Cairo, Egypt

To cite this Article Zayed, M. F. , Hafez, T. S. , El-din, N. Khir and Hefny, E.(1991) 'THE PHOTOLYSIS OF 1,3,4-THIADIAZOLIDINE-2,5-DITHIONES IN PRESENCE AND IN ABSENCE OF SINGLET OXYGEN', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 1, 51 — 55

To link to this Article: DOI: 10.1080/10426509108038830

URL: http://dx.doi.org/10.1080/10426509108038830

Phosphorus, Sulfur, and Silicon, 1991, Vol. 57, pp. 51–55
Reprints available directly from the publisher
Photocopying permitted by license only

THE PHOTOLYSIS OF 1,3,4-THIADIAZOLIDINE-2,5-DITHIONES IN PRESENCE AND IN ABSENCE OF SINGLET OXYGEN

M. F. ZAYED, T. S. HAFEZ, N. KHIR EL-DIN and E. HEFNY
National Research Centre, Dokki, Cairo, Egypt

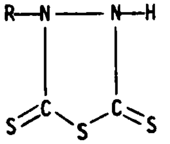
(Received May 15, 1990; in final form August 21, 1990)

The photolysis of 1,3,4-thiadiazolidine-2,5-dithiones (**Ia–c**) in methanol has been studied. The disulphides **IIa–c** were isolated and identified. Dye sensitized photooxygenation of compounds **Ia–c** were also studied. Compounds **IIa**, **IIIa** and **IVa** were produced in case of **Ia**, and **IIb** and **IIIb** were produced in **Ib**, and **IIc** and **IIIc** were produced in **Ic**. A mechanism for the formation of these compounds is presented.

Key words: 1,3,4-Thiadiazolidine-2,5-dithiones (**I**); bis-[5-thio-1,3,4-thiadiazolidinyl-(2)] disulfide (**IIa**); bis-[4-methyl-5-thion-1,3,4-thiadiazolinyl-(2)] disulfide (**IIb**); bis-[4-phenyl-5-thion-1,3,4-thiadiazolinyl-(2)] disulfide (**IIc**); bis-[4-methyl-5-oxo-1,3,4-thiadiazolinyl-(2)] disulfide (**IIIb**); bis-[4-phenyl-5-oxo-1,3,4-thiadiazolinyl-(2)] disulfide (**IIIc**); bis-[5-oxo-1,3,4-thiadiazolinyl-(2)] disulfide (**IIIa**); 2,5-dioxo-1,3,4-thiadiazolidine (**IVa**); photolysis; photooxygenation; methylene blue; singlet oxygen.

INTRODUCTION

In continuation of our previous studies on the photochemical behaviour of biologically active molecules,[1–5] it was of interest to investigate the photolysis of 1,3,4-thiadiazolidine-2,5-dithiones (**Ia–c**). These compounds have toxic effects as fungicides[6] and exhibit marked medicinal activities[7–9] as well as several industrial uses as photographic sensitizers[10] and adhesive materials.[11]



Ia, R = H
b, R = CH_3
c, R = C_6H_5

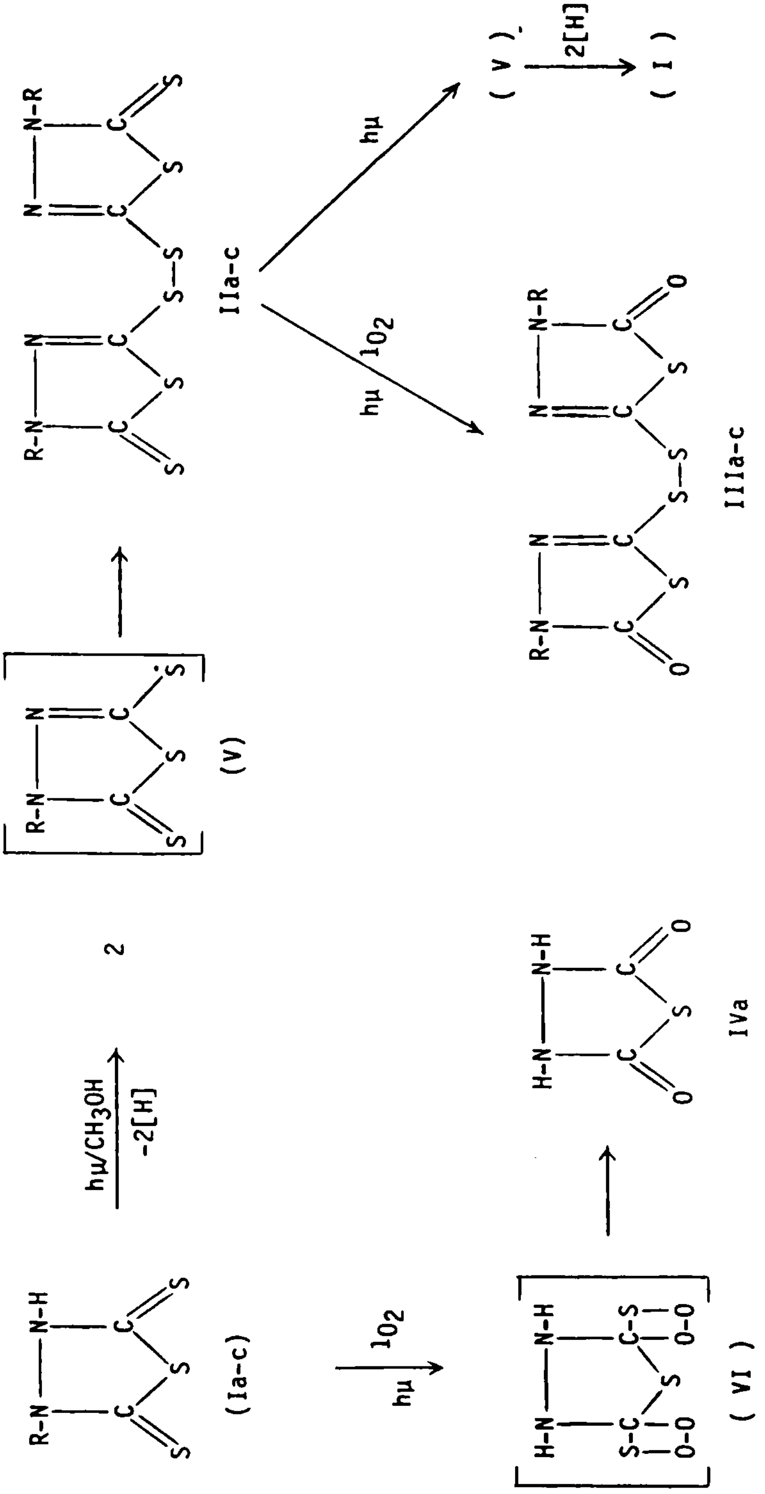
RESULTS AND DISCUSSION

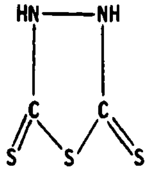
We have irradiated a 1% methanol solution of **Ia** with a Hg-high pressure lamp in a Pyrex vessel (λ > 315 nm). The photoreaction proceeded very slowly and bis-[5-thio-1,3,4-thiadiazolidinyl-(2)] disulfide (**IIa**) was formed in a low yield (20%) after 48 hours irradiation time and the starting compound (**Ia**) was recovered unchanged (80%). The photolysis of **Ia** was allowed to proceed in the presence of a sensitizer (methylene blue), while, oxygen (or normal air) was circulated in the mixture at a moderate rate. The reaction course was monitored by TLC for 6 hours and substantial reaction occurred. The photolysate was carefully chromatographed over silica gel and three compounds were isolated and identified as bis-[5-oxo-1,3,4-thiadiazolinyl-(2)] disulfide (**IIIa**), 2,5-dioxo-1,3,4-thiadiazolidine (**IVa**) and the disulfide **IIa**. The identities of products **IIa** and **IVa** were confirmed by physical measurements (IR, MS) and by comparison with authentic specimens (cf. experimental). Compound **IIIa**, was formulated due to the following: (1) Elemental analysis and molecular weight determination (MS) supported the molecular formula $C_4H_2N_4O_2S_4$ (m/e = 266). (2) The IR spectrum of compound **IIIa** shows a strong band at 1720 cm^{-1} due to the carbonyl absorption. The weak band observed at 510 cm^{-1} may be attributed to the absorption of the disulfide linkage. (3) Photooxygenation of compound **IIa** in methanol in presence of methylene blue produced **IIIa**.

Irradiation of **Ib** in methanol was investigated. Bis-[4-methyl-5-thion-1,3,4-thiadiazolinyl-(2)] disulfide (**IIb**) was formed in small yield. Bis-[4-phenyl-5-thion-1,3,4-thiadiazolinyl-(2)] disulfide (**IIc**) was also formed when **Ic** was irradiated under the same conditions. When these experiments were conducted in presence of methylene blue, bis-[4-methyl-5-oxo-1,3,4-thiadiazolinyl-(2)] disulfide (**IIIb**) and **IIb** were formed by irradiation of **Ib**, and bis-[4-phenyl-5-oxo-1,3,4-thiadiazolinyl-(2)]-disulfide (**IIIc**) and **IIc** were formed by irradiation of **Ic**. In both experiments no trace of compounds analogous to **IVa** was detected. The identities of compounds **IIb,c** and compound **IIIc** were confirmed by comparison with authentic samples, and the structure of compound **IIIb** was assigned from analytical and spectroscopic evidence.

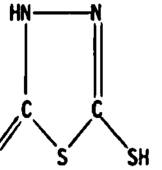
Carrying out the photooxygenation of **Ia–c** in the trace presence of 1,4-diazabicyclo(2,2,2)octane (DABCO) resulted in the recovery of the starting compounds. Only traces of the disulfides **IIa–c** could be detected after 100 hours irradiation time.

It is reasonable to explain the formation of products in presence of methylene blue by assuming the initial formation of both the thiyl radical (**V**) and the dioxathetain intermediate (**VI**). Recombination of the thiyl radicals led to the formation of the disulfide **II**, whereas, rupture of the C—S bond in the dioxathetain intermediate followed by ejection of SO resulted in the formation of **IV**. The formation of compound **III** in terms of subsequent oxidation of **II** by singlet oxygen via dioxathetain intermediate is most probable since photooxygenation of **II** in methanol produces **III** (vide supra). The presence of the starting compound (**I**) in a steady equilibrium with the disulfide **II** in the photolysate either in presence or in absence of methylene blue after a long period of irradiation could be explained by assuming a retro —S—S— cleavage of compound **II** into 2-thiyl radials which could abstract hydrogen to afford compound **I**. The absence of a compound analogous to **IVa** in the photolysate of both **Ib** and/or **Ic** indicate that the formation of the thiyl radicals in the presence of methylene blue is much faster than the formation of the dioxathetain intermediates. This is not surprising since substitution of alkyl groups for NH hydrogen in 2,5-dimercapto-1,3,4-thiadiazoles was known to force the molecule from the dithionic (**A**) to the thionic-thiolic (**B**) and to the dithiolic (**C**) forms.[12]

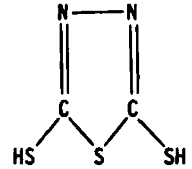

(Ia-c)
hμ/CH3OH
-2[H]
2
(V)
IIa-c
hμ
(V)
2[H]
(I)
hμ 1O2
IIIa-c
hμ 1O2
(VI)
IVa



A



B



C

The photooxygenation of compound **I** was quenched effectively by adding DABCO to the reaction mixture is in agreement with the above mechanism of the C═S → C═O transformations since DABCO quenched photoreactions proceed by singlet oxygen.[13]

EXPERIMENTAL

Melting points are uncorrected. The IR spectra were taken as KBr wafers in a Perkin-Elmer 157-G spectrophotometer. The mass spectra were taken at 70 eV on MAT 112 Mass Spectrophotometer using the direct inlet technique. The 1,3,4-thiadiazolidines (**Ia–c**) were prepared according to established procedures[14–16] and freshly recrystallized. Authentic specimens of compounds **IIa–c**, **IIIc** and **IVa** were prepared by known procedures[14,15,17] for direct comparisons (m.p., mixed m.p. as well as comparative TLC, IR and MS spectra). The TLC system used was toluene/ethylacetate/ethanol 6:1:1 (v/v/v). The photolysis were carried out in a pyrex photoreactor equipped with a high-pressure Hg lamp (Philips HPK/125).

Photolysis of **Ia–c** *in methanol. A solution of* **Ia** (1.5 g; 0.01 mole) in methanol (250 ml) was irradiated for 48 hrs. After evaporation of the solvent in vacuo, the mixture was separated by column chromatography on silica gel with pet. ether (40–60), and employing the eluent system pet. ether (40–60)—ethyl acetate (9:1). The first material eluted (1.2 g) was purified by recrystallization from ether as yellow crystals, m.p. 168°C, and shown to be starting material (**Ia**). The second material eluted (0.3 g) was recrystallized from ethanol as yellow crystals, m.p. 175°C, and identified as **IIa** (TLC), lit. m.p. 175°C; MS: m/e 298 (M^+); IR [1380 cm^{-1} (C═S); 460 cm^{-1} (—S—S—)].

Similar results have been obtained, when **Ib** (1.6g) was irradiated in methanol for 48 hrs. **Ib** was separated (1.2 g), m.p. and mixed m.p. 69°C (from ether) together with **IIb** (0.4g), m.p. 141°C (from chloroform-ethanol), lit. m.p. 141°C; MS: m/e 326 (M^+); IR [1375 cm^{-1} (C═S); 460 cm^{-1} (—S—S—)].

Similarly, irradiation of **Ic** (2.2 g) gave **IIc** (0.5 g), m.p. 124°C (from chloroform-ethanol), lit. m.p. 124–125°C, and the starting compound (**Ic**) (1.7 g), m.p. and mixed m.p. 90°C.

Photolysis of **Ia–c** *in methanol in pressure of singlet oxygen.* A solution of **Ia** (1.5 g) in methanol (250 ml) containing methylene blue (5 mg) was irradiated for 6 hour, while a steady stream of oxygen (or normal air) was circulated into the mixture at a moderate rate. After evaporation of the solvent in vacuo, the mixture was separated by column chromatography on silica gel with pet. ether (40–60) and was eluted first with pet. ether and then with petroleum ether containing increasing amounts of ethylacetate and at last by ethylacetate-ethanol mixture (1:1), the products were recovered by evaporating solvents. The first material eluted from the column melted at 175°C (0.15 g) and proved to be **IIa** (TLC). The second material eluted (0.8 g) was recrystallized from ethanol as orange crystals, m.p. 220°C and identified as **IVa** (TLC), lit. m.p. 222°C; MS: m/e 118 (M^+); IR [1740 cm^{-1} (C═O)]. The third material eluted (0.4 g) was recrystallized from ethanol as dark brown crystals, m.p. 280°C and identified as **IIIa**.

Irradiation of **Ib** (1.64 g) in a similar procedure gave **IIIb** (0.5 g) and **IIb** (0.8 g). Compound **IIIb** m.p. at 115°C, MS: m/e 294 (M^+); IR (1740 cm^{-1} (C═O); 480 cm^{-1} (—S—S—)].

Similarly, irradiation of **Ic** (2.3 g) gave **IIIc** (0.8 g) and **IIc** (1.2 g) compound **IIIc** m.p. at 78°C; lit. m.p. 78–79°C.

Photolysis of **IIa** *in methanol in presence of singlet oxygen.* A solution of **IIa** (3 g) in methanol (250 ml) containing 3 mg of methylene blue was irradiated for 24 hr, while oxygen (or normal air) was bubbled in the mixture. Working-up the reaction mixture as described above, resulted in the isolation of the unchanged **IIa** as a major constituent of the mixture. In addition 50 mg of compound **IIIa** was isolated and identified (m.p. and mixed m.p. 280°C).

Photolysis of **Ia–c** *in presence of DABCO.* A solution of **Ia** (1.5 g) in methanol (250 ml) containing methylene blue (5 mg) and DABCO (5 mg) was irradiated while oxygen was bubbling in the mixture for 100 hr. Detection by TLC indicated the presence of the starting compound (**Ia**) together with the disulfide **IIa**. Working up the reaction mixture as described, resulted in the isolation of 1.3 g of **Ia** and 0.1 g of **IIa**.

Similarly, **IIb** and/or **IIc** were separated as minor constituents from the photolysis of **Ib** and/or **Ic** under the same experimental conditions.

REFERENCES

1. M. F. Zayed, M. M. Sidky and H. Wamhoff, *Chemiker-Zeitung*, **109**, 231 (1985).
2. A. Nada, M. F. Zayed and Z. Refae, *Egypt. J. Chem.*, **28**, 439 (1985).
3. A. Nada, M. F. Zayed and E. Hefny, XIIth International Conference on Photochemistry, Tokyo-Japan 1985 (p. 621).
4. M. F. Zayed, N. Kh. Eldin and E. M. Kamel, *Egypt. J. Chem.*, **29**, 685 (1986).
5. M. F. Zayed and F. H. Osman, Y. O. El-Khoshnieh and E. El-Hefny, *Egypt. J. Chem.*, 1989 (in press).
6. M. Pianka, *J. Sci. Food Agr.*, **19**, 502 (1968); C.A. **69**, 96586u (1968).
7. D. A. McGinty and W. G. Bywater, *J. Pharmacol.*, **85**, 14 (1945); C.A. **40**, 1596^2 (1946).
8. M. H. Raven and H. Schriewer, *Arznein. Forsch.*, **21**, 75 (1971); C.A. **75**, 40322m (1971).
9. G. Kallirtrates and U. Kallirtrutes, *Chem. Chron.*, **5**, 115(1976); C.A. **87**, 34221j (1977).
10. Gevaert-Agfa, N. V. Neth Appl. 6, 615, 207 (Cl. G03c), March 28, 1967; C.A. **67**,69444y (1967).
11. Mackay, A. Iian, Bharucha and R. Nonabhai (British Nonferrous Metals Research Assoc.), Brit. 1, 231, 590 (Cl. C08F), 12 May 1971; C.A. **75**, 37380y (1971).
12. G. D. Thorn, *Can. J. Chem.*, **38**, 1439 (1960).
13. N. J. Turro, "Modern Molecular Photochemistry," The Benjamin Cummings Publishing Co., 590 (1978).
14. M. Busch, B. **27**, 2518 (1894).
15. M. Busch and E. Ziegele, J. pr. [2] **60**, 51 (1899).
16. G. D. Thorn, *Can. J. Chem.*, **38**, 1439 (1960).
17. P. K. Guha and S. K. Ray-Choud-Hury, *J. Indian Chem. Soc.*, **5**, 172 (1928).