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Clean Photodecomposition of 1-Methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thiones to Carbodiimides Proceeds via a Biradical

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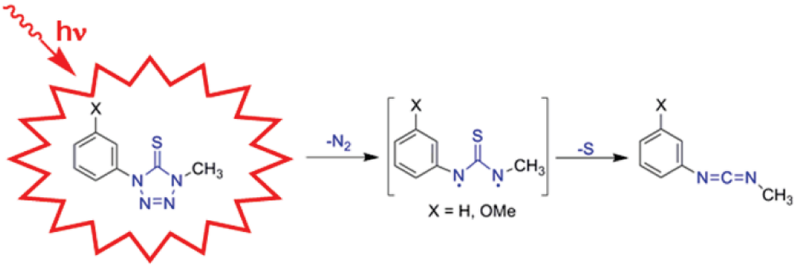

The photochemistry of 1-methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thione (**1a**) and 1-(3-methoxyphenyl)-4-methyl-1*H*-tetrazole-5(4*H*)-thione (**1b**) was studied in acetonitrile at 254 and 300 nm, which involves expulsion of dinitrogen and sulfur to form the respective carbodiimides **5a,b** as sole photoproducts. Photolysis of the title compounds in the presence of 1,4-cyclohexadiene trap led to the formation of respective thioureas, providing strong evidence for the intermediacy of a 1,3-biradical formed by the loss of dinitrogen. In contrast, a trapping experiment with cyclohexene provided no evidence to support an alternative pathway of photodecomposition involving initial desulfurization followed by loss of dinitrogen via the intermediacy of a carbene. Triplet sensitization and triplet quenching studies argue against the involvement of a triplet excited state. While the quantum yields for the formation of the carbodiimides **5a,b** were modest and showed little change on going from a C_6H_5 (**1a**) to *m*OMeC_6H_4 (**1b**) substituent on the tetrazolethione ring, the highly clean photodecomposition of these compounds to a photostable end product makes them promising lead structures for industrial, agricultural, and medicinal applications.

Introduction

Compounds containing a tetrazolethione scaffold have attracted attention as corrosion inhibitors,[1−3] pesticides,[4] stabilizers in photography,[5,6] UV resists in photolithography,[7] capping agents in semiconductor photocatalytic reactions,[8,9] and pharmaceutical agents.[10] Despite their widespread applications, studies on their structure and reactivity are limited, and a better understanding of the photochemistry of these ring systems is critical for designing compounds with improved performance. For instance, photostability of the tetrazolethione ring is of prime concern in exploiting these scaffolds for the synthesis of novel pesticides or pharmaceutical agents. It is therefore important to identify any unwanted phototoxic intermediates/products that may form upon UV exposure of these compounds and thus enable strategies for preventing those decomposition pathways and ensure greater photostability. On the other hand, in photolithography where tetrazolethione scaffolds have been proposed for the in situ photogeneration of carbodiimides that subsequently react with carboxylic acids to form deep UV resists,[7] high photolability of the tetrazolethione rings is

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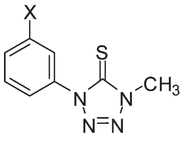
desirable, so that carbodiimides can be generated cleanly, quickly, and efficiently. Again, conclusive information about the various photochemical processes is required as the undesirable pathways may interfere with the formation of carbodiimides and therefore would need to be suppressed in order to increase the overall efficiency of the process.

There are a few reports in the literature that discuss the photochemistry of these heterocycles. For instance, work by Dunkin and co-workers in 1989 revealed that the photolysis of tetrazolethiones in a low-temperature matrix yields carbodiimides as a result of loss of dinitrogen and sulfur.[11] Several years later, the photochemistry of this ring system was revisited by Fausto et al., who reported that carbodiimides are not the only products in the gas phase and a variety of other photoproducts are formed.[12] The photolysis of 1-methyl-1*H*-tetrazole-5(4*H*)-thione in a low-temperature argon matrix was found to proceed via three decomposition pathways involving (1) the expulsion of dinitrogen to form 1-methyl-1*H*-diazirene-3-thiol, (2) the cleavage of the tetrazolethione ring to form methylisothiocyanate and the azide, and (3) the concurrent expulsion of dinitrogen and sulfur to form *N*-methyl carbodiimide.[12] The authors also reported that the primary photoproducts underwent further decomposition to form methyl diazene, carbon monosulfide, and nitrogen hydride.[12] However, in solution the photolysis of tetrazolethiones is known to form the corresponding carbodiimides or their tautomers as the sole products.[13-15]

To the best of our knowledge there are no reports on the mechanism of the photodecomposition of tetrazolethiones. A few mechanistic studies on the related tetrazolones are known.[16,17] For instance, Cristiano and co-workers studied the photochemistry of 1-allyl-4-phenyltetrazolones in solution that resulted in the formation of pyrimidinones as the major product, which underwent decomposition in nonalcoholic solvents to form secondary photoproducts such as allyl amine, aniline, phenyl isocyanate, and allyl isocyanate.[17] This photochemistry is believed to involve an intermediacy of a 1,3-triplet biradical formed via the elimination of molecular nitrogen from the photoexcited 1-allyl-4-phenyltetrazolones.[17] Cristiano also investigated the photochemistry of 5-allyloxy tetrazoles in solution and reported the formation of 1,3-oxazines as the sole primary photoproducts that undergo further reactions leading to the formation of hydrazines, enamines, aniline, and phenyl isocyanate.[16] Laser flash photolysis experiments further revealed that photodecomposition of 5-allyloxy tetrazoles involves the formation of triplet 1,3-biradicals.[16] We were interested in exploring if the mechanism of photodecomposition of tetrazolethiones also proceeds through a 1,3-biradical, analogous to the tetrazolones, or if another type of intermediate is involved. Therefore, we synthesized 1-methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thione (**1a**) and 1-(3-methoxyphenyl)-4-methyl-1*H*-tetrazole-5(4*H*)-thione (**1b**), investigated their photochemistry in acetonitrile, and gained preliminary insights into the mechanism of their photodecomposition (Scheme 1).

SCHEME 1. **1-Methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thiones 1a,b**

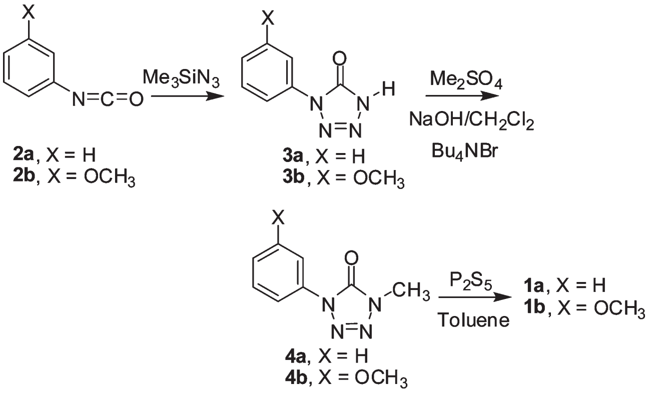


1a, X = H
1b, X = OCH_3

Results and Discussion

Synthesis of Tetrazolethiones 1a,b and Their Absorption Spectra. 1,3-Dipolar cycloaddition of phenylisocyanate (**2a**) with trimethylsilylazide resulted in the formation of 1-phenyl-1*H*-tetrazol-5(4*H*)-one (**3a**).[18] Compound **3a** was methylated with dimethyl sulfate to obtain the tetrazolone **4a**, which upon treatment with phosphorus pentasulfide yielded the desired 1-methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thione (**1a**).[19] Similarly, 3-methoxyphenylisocyanate (**2b**) was converted to **4b** as reported earlier,[20] which was subjected to thionation to obtain the desired 1-(3-methoxyphenyl)-4-methyl-1*H*-tetrazole-5(4*H*)-thione (**1b**) (Scheme 2).

SCHEME 2. **Synthesis of 1-Methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thiones 1a,b**



The UV spectral data of **1a** has been reported,[19] and the spectra of compound **1b** in cyclohexane, tetrahydrofuran, and acetonitrile are shown in Figure 1. Analogous to **1a**, four UV bands $\lambda_1-\lambda_4$ were observed for **1b** in cyclohexane and MeCN; however, λ_4 could not be observed in THF due to solvent interference (Figure 1). The corresponding values of molar absorptivities for these bands are shown in Table 1. λ_1 and λ_2 underwent slight blue shifts as the polarity of the solvent was increased from cyclohexane → THF → MeCN. λ_3 of **1b** remained unchanged, whereas λ_4 showed a blue shift from cyclohexane → MeCN. Time dependent density functional calculations revealed that all bands in **1a**[19] and **1b** result from $\pi \rightarrow \pi^*$ transitions with some degree of intramolecular

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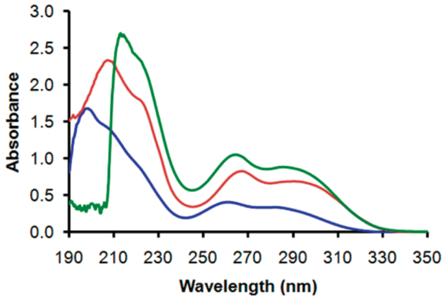


FIGURE 1. Absorption spectra of **1b** in cyclohexane (red), THF (green), and acetonitrile (blue).

TABLE 1. Energies (λ (E)) and Molar Absorptivities (log ε) for Peaks Observed in the Absorption Spectra of 1b in Cyclohexane, Tetrahydrofuran, and Acetonitrile

	cyclohexane		THF		MeCN	
	λ (E)[a]	log ε[b]	λ (E)[a]	log ε[b]	λ (E)[a]	log ε[b]
λ_1	290.0 (4.27)	3.82	285.0 (4.35)	3.97	281.0 (4.41)	3.82
λ_2	266.0 (4.66)	3.89	264.0 (4.69)	4.03	260.0 (4.77)	3.90
λ_3	222.0 (5.58)	4.31	223.0 (5.55)	4.40	221.0 (5.61)	4.34
λ_4	207.0 (5.98)	4.27			196.0 (6.32)	4.15

[a] In nm (eV). [b] In M^{-1} cm^{-1}

charge transfer (ICT) within the molecules (see Supporting Information for **1b**).

Product Analysis. The photolyses of argon-saturated solutions of **1a,b** in acetonitrile was carried out at 254 and 313 nm in a quartz cuvette. The UV spectral changes as a function of wavelength for compounds **1a** and **1b** at different irradiation times (as reported in the Experimental Section) are shown in Figures 2 and 3, respectively. The observance of clean isosbestic points in each case suggested the formation of a single photoproduct.

In order to identify the product(s), the photochemistry of argon-saturated solutions of **1a,b** in acetonitrile-d_3 was studied in a quartz NMR tube at 254 and 300 nm. The NMR spectrum of tetrazolethiones taken at different irradiation times indicated a clean photochemical reaction resulting into the formation of carbodiimides **5a,b** with the loss of dinitrogen and sulfur from the heterocyclic ring (Scheme 3, see Figures S4 and Figure S5 in Supporting Information). The NMR peaks corresponding to the respective carbodiimides were assigned by comparison of their chemical shift values to those of authentic samples. The formation of carbodiimides as the primary photoproduct was consistent with the result reported by Quast.[13−15] The photolyses were only carried out for 15 and 60 min at 254 and 300 nm, respectively. The

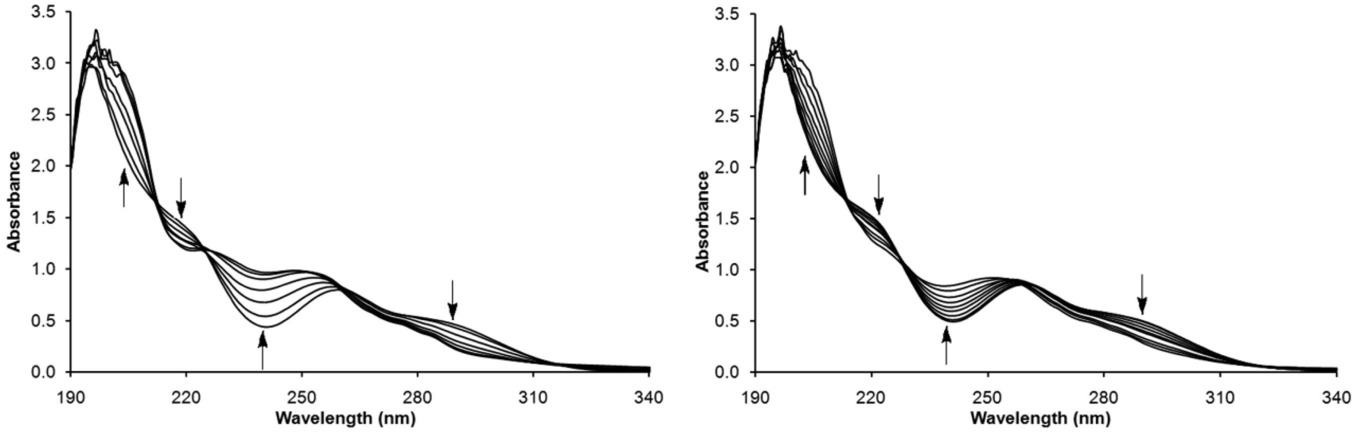


FIGURE 2. Changes in the UV spectrum of **1a** induced by irradiation at 254 (left) and 313 nm (right) in acetonitrile (arrows indicate the direction of spectral change upon irradiation).

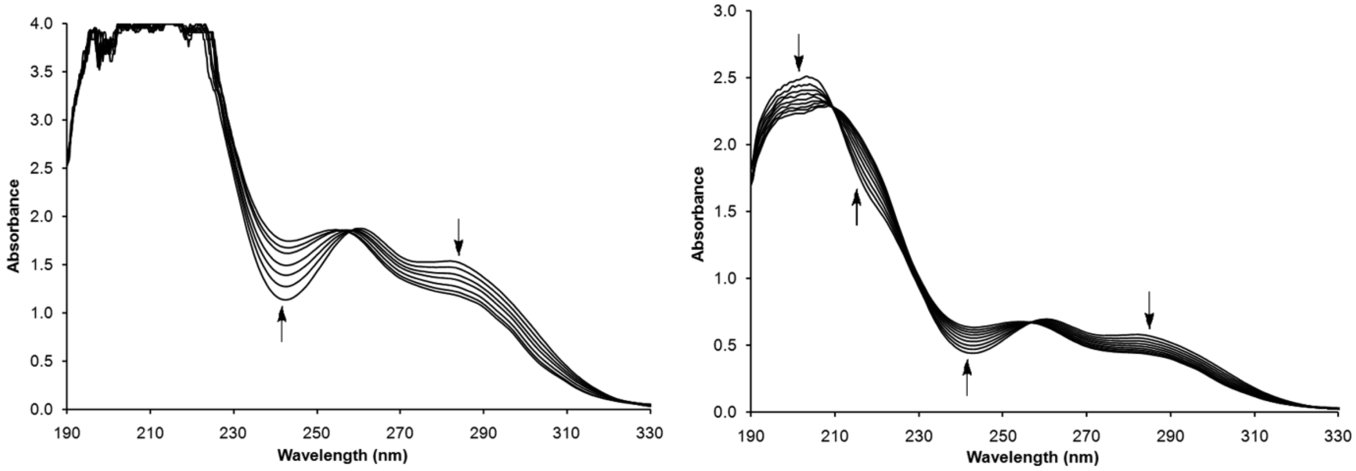


FIGURE 3. Changes in the UV spectrum of **1b** induced by irradiation at 254 (left) and 313 nm (right) in acetonitrile (arrows indicate the direction of spectral change upon irradiation).

SCHEME 3. Photochemical Conversion of Tetrazolethiones 1a,b to Carbodiimides 5a,b

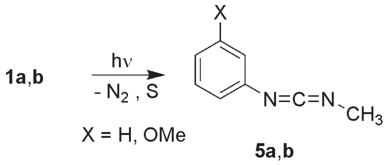


TABLE 2. Unreacted 1a,b (%), Products 5a,b (%), and Quantum Yields (Φ) for the Photodecomposition in MeCN

	λ	irradiation time		unreacted 1^a [%]	yield of 5^a [%]	Φ
1a	254	15	Ar-purged	57	44	0.045
		15	O_2-satd	55	47	
	300	60	Ar-purged	> 95	trace	
		60	O_2-satd	> 95	trace	
1b	254	15	Ar-purged	60	42	0.031
		15	O_2-satd	57	45	
	300	60	Ar-purged	> 95	trace	
		60	O_2-satd	> 95	trace	

[a] Amounts calculated by NMR spectroscopy with 1,4-dioxane as an internal standard (average of three irradiated samples). The standard deviation was in the range 0.4−2% and was calculated from three separate irradiated samples in each case.

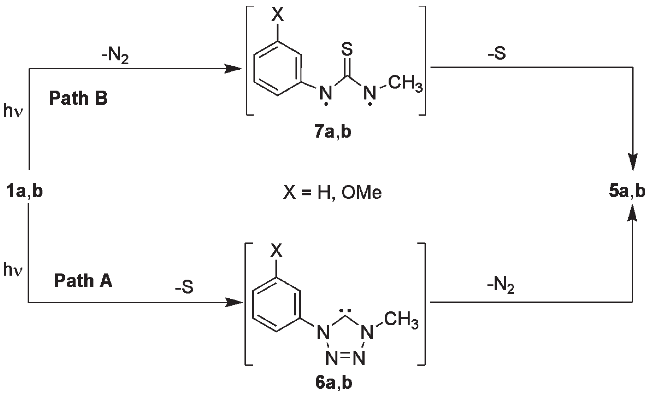
amount of **1a,b** that remained unreacted after irradiation and yields of corresponding products **5a,b** are listed in Table 2. There were trace amounts of other photoproducts (< 5%) that also formed during the photolysis of **1a,b** at 254 nm (see Figures S4 and S5 in Supporting Information). Their chemical shift values suggest that these may correspond to methyl isothiocyanate, corresponding aryl azides or benzimidazolethiones formed from the photodecomposition of **1a,b**. Note that these type of photoproducts have been previously detected in the photolysis of tetrazolethiones in the gas phase[12] as well as in the photodecomposition of their 5-*oxo* derivatives.[21] Only trace amounts of **5a,b** were formed after 60 min of exposure to 300 nm UV light. This was attributed to the low molar absorptivities of **1a,b** at that irradiation wavelength.

The quantum yields for the formation of **5a,b** were determined at 254 nm by using the azoxybenzene actinometer[22] and are reported in Table 2. Overall, the quantum yields were found to be modest, which indicates that the compounds might be involved in radiationless decay or fluorescence.

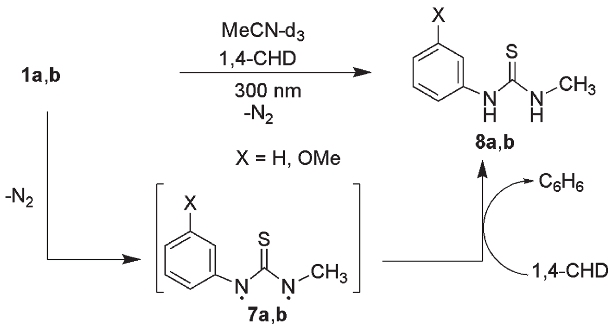
Furthermore, we investigated the formation of secondary photoproducts by irradiating the authentic samples of **5a,b** in acetonitrile-d_3 at 254 nm. The NMR spectrum recorded at 120 min of irradiation showed no decomposition, thus indicating that carbodiimides were stable photoproducts. This end product photostability is a desirable feature from an applications standpoint.

Mechanism of Photodecomposition. The formation of carbodiimides **5** from tetrazolethiones **1** involves the loss of dinitrogen and sulfur. Therefore, there are two possible photodecomposition pathways that must be considered: Path A, which involves desulfurization followed by elimination of dinitrogen, and path B, which involves the expulsion of dinitrogen followed by desulfurization (Scheme 4). The former pathway will involve the formation of a heterocyclic carbene **6** as intermediate, whereas the latter will lead to the formation of biradical **7** as the reactive species. In order to distinguish between these two mechanistic pathways, we carried out the experiments described below.

SCHEME 4. Two Possible Mechanistic Pathways for the Photodecomposition of 1a,b



SCHEME 5. Formation of Thioureas 8a,b during the Photolysis of 1a,b in the Presence of 1,4-CHD via the Intermediacy of 1,3-Biradical 7a,b



Investigating the Intermediacy of a Carbene. In order to explore the intermediacy of a heterocyclic carbene **6** in the photodecomposition, we carried out the photolyses of argon-purged solutions of **1a** and **1b** in acetonitrile-d_3 containing an excess of cyclohexene at 254 and 300 nm. The expectation was that if photochemistry took place through the intermediacy of a carbene, it could be trapped by cyclohexene to form the typical carbene addition product. However, analyses of the crude reaction mixture by NMR spectroscopy and ESI-MS/MS did not indicate the formation of product corresponding to the trapped carbene.

Investigating the Intermediacy of a Biradical. Next, we considered the possibility that the photochemistry could proceed through the intermediacy of a 1,3-biradical. The photolyses of argon-purged solutions **1a,b** in acetonitrile-d_3 were carried out in the presence of a hydrogen atom donor, 1,4-cyclohexadiene (1,4-CHD), at 300 nm. We predicted that if the photoreaction of **1a,b** occurred through the intermediacy of a biradical, it could be trapped by 1,4-CHD prior to expulsion of sulfur, yielding a thiourea reduction product. Indeed, the NMR spectroscopic analyses of the reaction mixture indicated the formation of thioureas **8a,b** as major product (Scheme 5). In addition,

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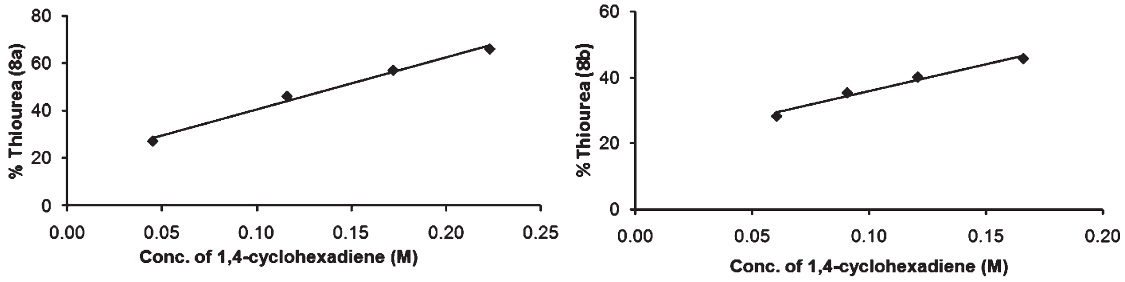

FIGURE 4. Plot showing an increase in the amount of thioureas **8a** (left) and **8b** (right) with an increase in the concentration of 1,4-CHD during the photolysis of **1a** and **1b** in acetonitrile, respectively.

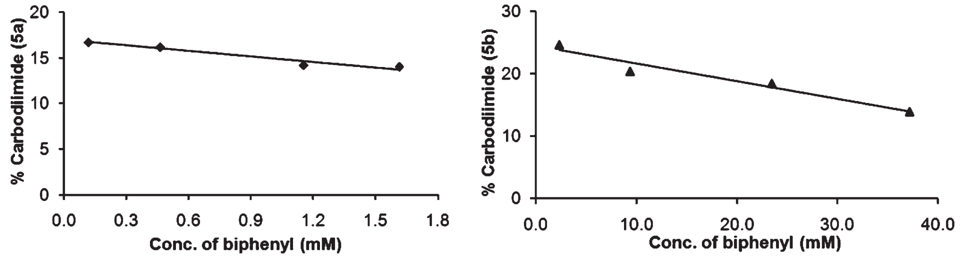

FIGURE 5. Modest quenching of carbodiimides **5a** (right) and **5b** (left) during the photolysis of **1a** and **1b** in the presence of biphenyl, respectively.

trace amounts of the respective carbodiimides **5a,b** were also formed. Our studies demonstrated that as the concentration of 1,4-CHD was increased the yield of thiourea also increased (Figure 4). The formation of thioureas **8a,b** as the major products during the photolysis of **1a,b** in the presence of 1,4-CHD is suggestive of the intermediacy of a 1,3-biradical **7a,b** in the photodecomposition of the title compounds. While this trapping experiment strongly implicates the intermediacy of a biradical, it does not provide definitive evidence for whether the biradical exists in its triplet or singlet spin multiplicity. However, since singlet biradicals are known to be extremely short-lived,[23,24] in all probability the trapped species is the triplet biradical since these have lifetimes long enough to react with externally added traps.[25] In addition, desulfurization from a triplet biradical **7a,b** to produce carbodiimide **5a,b** will yield a ground state triplet sulfur atom (^3P)[26] that is energetically more favorable than desulfurization from a singlet biradical **7a,b**, which will lead to the formation of an excited state singlet sulfur atom (^1D). We believe that the lost sulfur atoms become S_8 as this is the most common allotrope of sulfur.[27] This argument is further supported by the yellow coloration of the reaction mixture produced after photolysis, which is suggestive of S_8 formation.

Investigating the Involvement of a Triplet Excited State. Since the 1,4-CHD trapping experiments were suggestive of a triplet biradical intermediate, a plausible precursor to such a species would be the triplet excited state of the photoprecursor **1a,b**. In order to explore the possibility of photochemistry from a triplet excited state, we irradiated argon-purged solutions of **1a,b** in acetonitrile-d_3 at 300 nm in the presence of triplet sensitizers of varying energies (e.g., benzophenone, acetophenone, and acetone). The analyses of the reaction mixture by NMR spectroscopy after 60 min of irradiation revealed that no carbodiimides **5a,b** were formed, and therefore no photosensitization was observed. In order to rule out the possibility of high lying triplet state, we also performed the photolyses at 300 nm in the presence of a triplet quencher, e.g., biphenyl (Figure 5). Our results indicate that as the concentration of biphenyl was increased, the yields of carbodiimide were only slightly decreased. This minimal decrease in the yield of photoproduct in the presence of a quencher could be explained by a slight competitive absorption of the quencher at 300 nm. Photolyses of the oxygen-saturated solutions of **1a,b** in acetonitrile-d_3 were also carried out at 254 and 300 nm. The conversion of the tetrazolethiones and the product yields were found to be almost identical to those of the argon-saturated solutions, indicating that the effect of the oxygen on the photochemistry of tetrazolethiones was negligible (Table 2).

The inability to detect any photoproducts during triplet sensitization of **1a,b**, as well as only a modest inhibition of carbodiimide formation observed in the triplet quenching experiments with biphenyl, does not provide strong support for the intermediacy of a triplet excited state. Given that our computations indicate that the excited state of **1a,b** is of π,π^* nature[19] (Supporting Information), this may be due to a slow rate of intersystem crossing relative to singlet bond scission ($^1\pi,\pi^* \rightarrow {}^3\pi,\pi^*$ intersystem crossings are frequently slowed as a result of this being a spin−orbit coupling "forbidden" conversion[28]). Although negative results do not provide conclusive evidence, dissociation of dinitrogen from the singlet excited state seems more plausible.

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Conclusions

We have reported a clean photoconversion of 1-methyl-4-phenyl-1*H*-tetrazole-5(4*H*)-thione (**1a**) and 1-(3-methoxyphenyl)-4-methyl-1*H*-tetrazole-5(4*H*)-thione (**1b**) to the corresponding photostable carbodiimides **5a,b**. Analogous to the 5-*oxo* derivatives of tetrazoles, the photodecomposition 5-*thio* derivatives occurs via the intermediacy of a 1,3-biradical **7a,b**, which is believed to be in its triplet spin multiplicity. We find no evidence for an alternative pathway involving a carbene, wherein desulfurization occurs prior to loss of dinitrogen. We were further interested in identifying the nature of precursor that leads to this biradical. The photosensitization and triplet quenching experiments argue against the involvement of a triplet excited state. The obvious alternative mechanistic pathway that could lead to the formation of a 1,3-triplet biradical is a diradicaloid species generated directly from the singlet excited state of **1a,b** after the expulsion of dinitrogen. Once formed, this diradicaloid species could be envisioned to undergo intersystem crossing to generate the triplet biradical **7a, b** which then would undergo desulfurization to form **5a,b**.

Overall, these studies indicate that **1a** and **1b** are highly promising lead compounds for industrial, agricultural, and medicinal applications. The search for derivatives with improved quantum yields that retain the clean photochemistry and end-product photostability of **1a,b** would be of considerable interest. Our mechanistic studies suggest that derivatives should be sought that favor dinitrogen dissociation in the excited state, since this appears to be the favored pathway in the photodecomposition of these compounds.

Experimental Section

General Procedures. Thin layer chromatography was carried out on 250 μm silica gel plates, and UV light was used as a visualizing agent. Standard column chromatography was performed using 63−200 μm silica gel. ^{1}H and ^{13}C NMR spectra for the structural characterization of the compounds were recorded on 400 MHz NMR spectrometer. The carrier frequencies were 399.75 MHz (^{1}H) and 100.53 MHz (^{13}C). The number of scans used was 64 for ^{1}H NMR spectra and for ^{13}C, ranging from 3−5 K depending on the sample concentration. Both the ^{1}H and ^{13}C spectra were recorded with longer relaxation time (10 s). Chemical shifts and the coupling constants are reported in parts per million and Hertz, respectively. All the quantitative analyses of the photolyzed reaction mixtures were performed by NMR spectroscopy with 1,4-dioxane as an internal standard.[29] These experiments were carried out on a 500 MHz NMR spectrometer equipped with a 3 mm triple resonance inverse detection pulse field gradient probe operating at 499.848 MHz for ^{1}H. The spectra were an accumulation of 64 individual scans. The photoproducts were assigned by comparison of their chemical shift values to that of authentic samples. The infrared frequencies are reported in cm^{-1}. High resolution mass spectra were acquired on a quadrupole/time-of-flight mass spectrometer. The samples were prepared in methanol/acetonitrile (containing 0.1% formic acid in some cases) and were introduced by continuous infusion into the electrospray ionization (ESI) source at a rate of 30 μL/min. TOF scans were carried out in positive ionization mode. In most cases, both $[M + H]^+$ and $[M + Na]^+$ ions were detectable for each species. All irradiations were carried out in a Rayonet reactor at 254 nm and broad band 300 nm UV light. Monochromatic 313 nm was obtained by using broad band 300 nm UV lamps and by filtering the radiation through a solution of 0.002 M K_2CrO_4 in 5% Na_2CO_3.

Note that the syntheses of **1a,b** require $TMSN_3$ and Me_2SO_4; extreme caution must be taken during the handling of these reagents because of their hazardous nature.

1-(3-Methoxyphenyl)-4-methyl-1*H*-tetrazole-5(4*H*)-thione (1b). P_2S_5 (1.3 g, 5.8 mmol) was added to a solution of **4b** (0.5 g, 2.4 mmol) in dry toluene (15 mL). The mixture was refluxed at 110 °C until the starting material disappeared. The reaction mixture after filtration was concentrated under reduced pressure. Purification by column chromatography (SiO_2, hexane/ethyl acetate, 93:7) gave **1b** (0.42 g, 78% yield) as a white solid: R_f 0.64 (70:30 hexane/ethyl acetate); mp 52−54 °C; FTIR (ATR) 1600, 1590, 1492, 1440, 1356, 1324, 1238, 1195, 1160, 1065, 1022, 865, 839, 782, 681. ^{1}H NMR (400 MHz, CD_3CN): δ 7.53 (s, 1H), 7.51−7.49 (m, 1H), 7.46−7.43 (m, 1H), 7.13−7.10 (m, 1H), 3.89 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 165.0, 161.0, 137.0, 131.2, 117.2, 116.2, 111.0, 56.4, 35.5. HRMS: exact mass calculated for $(M + H^+)$ $C_9H_{11}N_4OS^+ = 223.0654$, found 223.0648; $(M + Na^+)$ $C_9H_{10}N_4OSNa^+ = 245.0473$, found 245.0468.

Spectroscopic Data. 1-Phenyl-1*H*-tetrazol-5(4*H*)-one (3a)[18,19]**.** White solid (1.67 g, 82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 7.68 Hz, 2H), 7.56 (t, J = 7.60 Hz, 2H), 7.42 (t, J = 7.51 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 150.2, 134.1, 129.4, 127.5, 119.5.

1-Methyl-4-phenyl-1*H*-tetrazol-5(4*H*)-one (4a)[19]**.** Crystalline solid (0.30 g, 91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 8.27 Hz, 2H), 7.58 (t, J = 7.03 Hz, 2H), 7.44 (t, J = 7.40 Hz, 1H), 3.62 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6): δ 148.8, 134.2, 129.5, 127.7, 119.4, 31.2.

4-Methyl-1-phenyl-1*H*-tetrazole-5(4*H*)-thione (1a)[19]**.** Yellow solid (2.30 g, 53%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.89−7.85 (m, 2H), 7.63−7.55 (m, 3H), 3.89 (s, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 165.1, 136.2, 130.8, 130.3, 125.3, 35.5.

1-(3-Methoxyphenyl)-1*H*-tetrazol-5(4*H*)-one (3b)[20]**.** Pale white solid (0.52 g, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6): 7.47−7.41 (m, 3H), 6.98 (d, J = 4 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6): 159.8, 150.2, 135.3, 130.4, 113.0, 111.3, 105.0, 55.4.

1-Methyl-4-(3-methoxyphenyl)-1*H*-tetrazol-5(4*H*)-one (4b)[20]**.** Crystalline solid (0.50 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.49 − 7.43 (m, 3H), 7.15 (d, 1H), 3.81 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6): 159.8, 148.7, 135.3, 130.6, 113.2, 111.3, 105.0, 55.5, 31.3.

The synthesis of the authentic samples is described below.

1-Methyl-3-phenylthiourea (8a)[30]**.** Prepared by a slight modification of the previously reported procedure. To a solution of aniline (1.5 g, 16.1 mmol) in methanol (75 mL) was added methylisocyanate (1.3 g, 17.7 mmol), and the reaction mixture was stirred at 65 °C for 24−30 h. After the completion of the reaction, solvent was removed by distillation under reduced pressure to obtain crude product. Recrystallization in ethanol yielded **8a** (2.46 g, 92% yield) as white solid: R_f 0.29 (60:40 hexane/ethyl acetate); mp 110−112 °C; FTIR (ATR) 3259, 3155, 2989, 2937, 1515, 1490, 1287, 1246, 1210, 1026, 1001, 723, 689, 640, 602. ^{1}H NMR (400 MHz, CD_3CN): δ 8.12 (s, 1H), 7.41−7.37 (m, 1H), 7.29−7.22 (m, 3H), 6.56 (s, 1H), 2.97 (d, J = 8 Hz, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 182.8, 138.7, 130.4, 127.0, 126.0, 32.1. HRMS: exact mass calculated for $(M + H^+)$ $C_8H_{11}N_2S^+ = 167.0643$, found 167.0637; $(M + Na^+)$ $C_8H_{10}N_2SNa^+ = 189.0462$, found 189.0457.

1-(3-Methoxyphenyl)-3-methylthiourea (8b)[31]**.** Prepared as previously reported.[31] White solid (2.1 g, 87% yield); mp 98−100 °C. ^{1}H NMR (400 MHz, CD_3CN): δ 8.06 (s, 1H), 7.29 (t, 1H), 6.88−6.78 (m, 3H), 6.62 (s, 1H), 3.78 (s, 3H), 2.97 (d, J = 8 Hz, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 182.7, 161.5, 139.7, 131.3,

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117.7, 112.5, 111.4, 56.1, 32.2. HRMS: exact mass calculated for $(M + H^+)$ $C_9H_{13}N_2OS^+ = 197.0749$, found 197.0743; $(M + Na^+)$ $C_9H_{12}N_2OSNa^+ = 219.0568$, found 219.0563.

***N*-((Methylimino)methylene)aniline (5a).** Prepared by a different method than previously reported.[32] Mercuric oxide (3.9 g, 18.1 mmol) was added to a solution of **8a** (1.0 g, 6.0 mmol) in CH_2Cl_2/H_2O (4:1, 30 mL), and the mixture was stirred at room temperature for 30 min. The reaction mixture was filtered through Celite and washed with ample amounts of methylene chloride. The filterate was concentrated under reduced pressure. Purification by column chromatography (SiO_2, hexane/ethyl acetate, 95:5) gave **5a** (0.1 g, 12% yield) as a yellow oil: R_f 0.83 (70:30 hexane/ethyl acetate); FTIR (ATR) 3059, 3024, 2935, 2879, 2121, 2026, 1592, 1499, 1406, 1282, 1156, 1070, 891. ^1H NMR (400 MHz, CD_3CN): δ 7.33−7.29 (t, 2H), 7.14−7.09 (m, 3H), 3.14 (s, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 142.0, 137.0, 130.5, 125.6, 124.4, 32.8. HRMS: exact mass calculated for $(M + H^+)$ $C_8H_9N_2^+ = 133.0766$, found 133.0760.

3-Methyl-*N*-((methylimino)methylene)aniline (5b). Similarly, compound **5b** (0.35 g, 42% yield) was obtained from **8b** (1.00 g, 5.1 mmol). Purification by column chromatography (SiO_2, hexane/ethyl acetate, 95:5) gave **5b** (0.35 g, 42% yield) as a yellow oil: R_f 0.71 (70:30 hexane/ethyl acetate); FTIR (ATR) 2937, 2834, 2123, 1594, 1581, 1493, 1464, 1421, 1281, 1243, 1127, 1038, 945, 840, 769, 684 589. ^1H NMR (400 MHz, CD_3CN): δ 7.20 (t, 1H), 6.70 - 6.63 (m, 3H), 3.76 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (400 MHz, CD_3CN): δ 161.6, 143.2, 136.7, 131.1, 116.7, 111.3, 109.9, 56.0, 32.8. HRMS: exact mass calculated for $(M + H^+)$ $C_9H_{11}N_2O^+ = 163.0871$, found 163.0866.

Photochemistry. UV Spectral Changes. An argon-purged solution of **1a** (0.07 mM) and **1b** (0.13 mM) in acetonitrile was irradiated in a quartz cuvette at 254 nm. In the case of **1a**, a UV spectrum was obtained after each irradiation at 0, 20, 40, 60, 120, 200, 300, and 420s, whereas in the case of **1b**, a UV spectrum was obtained after each irradiation at 0, 20, 40, 60, 80, 120, and 150s, respectively. Similarly, the irradiation of an argon-purged solution of **1a** (0.2 mM) and **1b** (0.075 mM) in acetonitrile was carried out in a quartz cuvette at 313 nm, and a UV spectrum was obtained after irradiation at different time intervals (at 0, 1, 5, 10, 15, 20, 30, 40, and 50 min for **1a** and 0, 5, 10, 15, 20, 25, 25, 30, 35, and 40 min for **1b**).

Product Analysis. An argon-purged solution of **1a,b** (0.45 mL) in acetonitrile-d_3 (approximately in the range 4.63 mM) was irradiated in a quartz NMR tube at 254 and 300 nm, and a NMR spectrum was obtained at every 5 min time interval for 15 and 60 min, respectively.

Photolysis of Carbodiimides 5a,b. An argon-purged solution of **5a,b** (0.7 mL) in acetonitrile-d_3 (approximately in the range 4.70 mM) was irradiated in a quartz NMR tube at 254 for 120 min, and a NMR spectrum was obtained.

Photolysis in the Presence of Cyclohexene. An argon-purged solution of **1a,b** (0.7 mL) in acetonitrile-d_3 (approximately in the range 4.55 mM) containing 10 equiv of cyclohexene was irradiated at 254 and 300 nm in a quartz NMR tube for 30 and 60 min, respectively, and a NMR spectrum was obtained. For the ESI-MS/MS experiments, the concentration of **1a** and **1b** was in the range 1.5 mM. Eight milliliters of this solution was irradiated at 254 and 300 nm. The solvent was removed on a rotary evaporator and crude was analyzed.

Photolysis in the Presence of 1,4-Cyclohexadiene. Four separate solutions of **1a,b** (approximately in the range 4.63 mM) in acetonitrile-d_3 (0.7 mL) containing varying amounts of 1,4-CHD (10−50 equiv) were taken in quartz NMR tubes. The mixture in each tube was purged with argon for 15 min and irradiated with broad band 300 nm UV lamp for 60 min, and a NMR spectrum was recorded.

Photosensitization and Triplet Quenching. The concentration of **1a** and **1b** for the following experiments was approximately 4.63 mM in acetonitrile-d_3.

Three separate solutions of **1a,b** (0.7 mL) in acetonitrile-d_3 containing benzophenone, acetophenone, and acetone (1−20 equiv), respectively, were taken in quartz NMR tubes, purged with argon for 15 min, and irradiated with broad band 300 nm UV lamp for 60 min. Subsequently, a NMR spectrum was obtained.

Four separate solutions of **1a,b** in acetonitrile-d_3 (0.7 mL) containing varying amounts of biphenyl (0−15 equiv) were taken in different quartz NMR tubes. The mixture in each tube was purged with argon for 15 min and irradiated with broad band 300 nm UV lamp for 60 min, and NMR spectrum was recorded.

Effect of Oxygen. An oxygen-purged solution of **1a,b** (0.65 mL) in acetonitrile-d_3 (approximately in the range 4.63 mM) was irradiated in a quartz NMR tube at 254 and 300 nm for 15 and 60 min, respectively, and NMR spectrum was recorded.

Actinometry. A 5.04 mM solution of azoxybenzene in 95% ethanol and a 0.1 M solution of KOH in 95% ethanol were prepared. The azoxybenzene solution was irradiated for 30 min in a quartz cuvette at 254 nm (no purging with Ar required), and 1 mL of the irradiated solution was mixed with 1 mL of 0.1 M KOH solution followed by the addition of 8 mL of 95% EtOH in a volumetric flask. A UV spectrum was subsequently recorded, and the incident photons were calculated in mol/L/s as described by Bunce et al.[22] The quantum yields were calculated at less than 10% conversions.

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Supporting Information Available: Theoretical calculations on the electronic properties of **1b**; computational methods; resonance structures of **1b** (Scheme S1); ground state geometry of **1b** (Figure S1); Cartesian coordinates for the optimized **1b**; experimental absorption spectra and TDDFT calculated vertical excitations as stick spectra for **1b** in cyclohexane, THF and acetonitrile (Figure S2); molecular orbitals for the optimized geometries of **1b** in acetonitrile (Figure S3); TDDFT calculated vertical excitation energies, oscillator strengths, MO character and transition type of **1b** in cyclohexane, THF and acetonitrile (Tables S1); NMR spectra of **1a,b** before and after irradiation at 254 nm (Figures S4 and S5); ^1H NMR and ^{13}C NMR spectra of **1b** and **5b**; ^1H NMR spectra of **5a** and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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